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(54) Title: ELECTROLUMINESCENT LAMINATE WITH PATTERNED PHOSPHOR STRUCTURE AND THICK FILM DIELECTRIC WITH IMPROVED DIELECTRIC PROPERTIES			
(57) Abstract			
<p>A patterned phosphor structure, and EL laminate containing same (10), forming red, green and blue sub-pixel phosphor elements (30) for an AC electroluminescent display. The patterned phosphor structure includes at least a first (30) and a second phosphor (22) emitting light in different ranges of the visible spectrum, but with combined emission spectra contains red, green and blue light, the first (30) and second phosphors (22) being in a layer, arranged in adjacent, repeating relationship to each other to provide a plurality of repeating first and second phosphor deposits. The phosphor structure also includes one or more means (25) associated with one or more of the first and second phosphor deposits, and which together with the first and second phosphor deposits, form the red (30a), green (30c) and blue (30b) sub-pixel phosphor elements, for setting and equalizing the threshold voltages, and for setting the relative luminosities. Also provided is an improved dielectric layer (16) for use in an EL laminate.</p>			
<p>The diagram illustrates the cross-section of an EL laminate. It shows a stack of layers: 12, 14, 16, 18, 22, 24, 26, and 30. Layer 30 is labeled with arrows pointing to sub-pixel structures 30a, 30b, and 30c. Layer 22 is labeled with arrows pointing to 30a and 30b. Layer 16 is labeled with an arrow pointing to 30c. Layer 18 is labeled with an arrow pointing to the interface between 16 and 22. Layer 24 is labeled with an arrow pointing to the interface between 22 and 26. Layer 26 is labeled with an arrow pointing to the interface between 24 and 10. Layer 10 is labeled with an arrow pointing to the top surface.</p>			

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**ELECTROLUMINESCENT LAMINATE WITH PATTERNED PHOSPHOR
STRUCTURE AND THICK FILM DIELECTRIC WITH IMPROVED
DIELECTRIC PROPERTIES**

FIELD OF THE INVENTION

This invention relates to AC electroluminescent (EL) devices fabricated using thin film and/or thick film technologies. The invention also relates to full colour EL devices.

BACKGROUND OF THE INVENTION

U.S. Patent 5,432,015, issued July 11, 1995, to Wu et al., and U.S. Patent 5,756,147, issued May 26, 1998, to Wu et al. disclose an electroluminescent laminate structure which combines a thick film dielectric layer with thin film layers, and a rear to front method of forming same on a rigid, rear substrate. Solid state displays (SSD) using this hybrid thick film/thin film technology have been demonstrated to have good performance and brightness (luminosity) in monochrome (ZnS:Mn phosphor) and full colour (ZnS:Mn/SrS:Ce bilayer phosphor) applications (Bailey et al., SID 95 Digest, 1995), however, improvements are still needed.

The potential for EL as a competitive alternative for fabricating flat panel displays has been hindered by the inability to generate bright, stable full colour. This has resulted in EL only penetrating markets for niche applications, in which the inherent benefits of the technology, such as ruggedness, wide viewing angle, temperature insensitivity, and fast time response, are needed.

Two basic alternatives have been used to produce full colour EL devices. One approach is to use patterned phosphors, that is alternating red, green and blue (RGB) phosphor elements in a layer (see for example U.S. Patent 4,977,350, issued December 11, 1990, to Tanaka et al.). This approach has the disadvantage of requiring the three phosphors to be patterned into red, green and blue sub-pixels that make up each pixel, in separate steps. Furthermore, the three colours cannot all be produced brightly enough by currently available EL phosphors to gain the brightness advantage desired. A second approach is to use a colour by white technique, first described by Tanaka et al., (SID 88 Digest, p 293, 1988, see also, U.S. Patent 4,727,003, issued February 23, 1988 to Ohseto et al.). In the colour by white method, the phosphor layer comprises layers of phosphors, typically ZnS:Mn and SrS:Ce, which when superimposed produce white light. Red, green and blue sub-pixels are then

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1 obtained by placing a patterned filter in front of the white light. The white phosphor emits
2 light at wavelengths over the entire visible portion of the electromagnetic spectrum, and the
3 filters transmit a narrowed range of wavelengths corresponding to the colours for each sub-
4 pixel. This approach has the disadvantage of relatively poor energy efficiency, in high
5 measure because a high fraction of the light is absorbed in the filters and the overall energy
6 efficiency of the display is correspondingly reduced.

7 Another requirement for full colour displays is gray scale capability, that is the ability
8 to generate a number of defined and consistent luminosities (light emission intensities) for
9 each sub-pixel. Typically, 256 gray scale luminosities span a range from zero to full
10 luminosity controlled by predetermined input electrical signals for each sub-pixel. This
11 number of gray levels provides a total of about 16 million individual colours.

12 Electroluminescent displays have pixels and sub-pixels that are defined by
13 intersecting sets of conductor stripes at right angles to one another on opposite sides of a
14 phosphor layer. These sets of stripes are respectively referred to as "rows" and "columns".
15 The sub-pixels are independently illuminated using an addressing scheme called passive
16 matrix addressing. This entails sequentially addressing the rows by applying a short flat-
17 topped electrical pulse with a peak voltage called the threshold voltage sequentially on each
18 of the rows such that the duration of the pulse is less than the time allocated for addressing
19 each row. Electrical pulses, each with a defined and independent peak voltage, termed the
20 "modulation voltage", are simultaneously applied to each of the columns intersecting the
21 addressed row. This provides independently controllable voltages across the sub-pixels
22 making up the pixels along that row, in accordance with the instantaneous luminosity
23 required for each sub-pixel to achieve the desired pixel colours. While each row is being
24 addressed, the remaining rows are disconnected, or are connected to a voltage level near zero.
25 Independent operation of all sub-pixels on the display requires that sub-pixels not on the
26 addressed row do not illuminate. The electro-optical characteristics of the sub-pixels on an
27 electroluminescent display facilitate meeting this requirement, by virtue of the fact that no
28 luminosity is generated if the voltage across the sub-pixels is below the threshold voltage.

29 The time required to address all the rows in a display is called a frame, and for video
30 images, the frame repetition rate must be at least about 50 Hz in order to avoid image flicker.
31 At the same time there is a maximum frame repetition rate, typically about 200 Hz, that is

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achievable due to a limitation on the voltage rise time associated with the electrical characteristics of the display and its associated electronics. In principle, a measure of gray scale can be achieved by controlling the average pixel luminosity by modulating the average frame rate. This requires omitting a fraction of the electrical pulses over a suitably short period of time. In practice, however, due to the limited range of frame rates, only a few levels of gray scale can be realized this way. Another option, called dithering, is to extinguish one or more pixels in the immediate vicinity of a pixel where reduced luminosity is required, thereby spatially modulating luminosity. This technique, however, causes a loss of display resolution and image quality.

The preferred method of gray scale control is to control the instantaneous sub-pixel luminosity, which must be done by modulating the electrical pulse peak voltage, pulse duration or pulse shape. At the same time, to minimize power consumption in electroluminescent displays addressed using passive matrix addressing, it is desirable to have the row voltage as close as possible to the threshold voltage above which luminosity is generated. This requires the threshold voltage for all sub-pixels to be equal.

Filters used to tailor the spectral emission characteristics of sub-pixels typically do not have ideal characteristics. They do not have perfect transmission in the desired wavelength ranges to achieve the desired red, green and blue colours, and they have some optical transparency in the wavelength ranges where they should be opaque. These deviations from ideal behavior impose design limitations on the overall pixel design. For example, the polymer based blue filters commonly used for electroluminescent and other types of flat panel displays have some transmission also in the red portion of the spectrum. The need to suppress red contamination of the blue pixel requires that thicker polymer films be used, which reduces the transparency in the desired blue wavelength range. They also have some transparency in the green wavelength range introducing a similar requirement for thicker polymers that are less transparent to blue light. To meet the requirements for full colour displays, the ratios of luminosity for red:green:blue sub-pixels should be 3:6:1, to give a white colour for that pixel. The CIE colour coordinates for red sub-pixels should be in the range $0.60 < x < 0.65$ and $0.34 < y < 0.36$. The CIE colour coordinates for green sub-pixels should be in the range $0.35 < x < 0.38$ and $0.55 < y < 0.62$. For blue sub-pixels the CIE colour coordinates should be in the range $0.13 < x < 0.15$ and $0.14 < y < 0.18$. The combined (white)

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1 luminosity for a pixel comprising red, green and blue sub-pixels should be at least about 70
2 candelas per square meter (cd/m^2) and the CIE colour coordinates for full white should be in
3 the range $0.35 < x < 0.40$ and $0.35 < y < 0.40$. Higher luminosity is desirable for some
4 applications.

5 Phosphors useful in electroluminescent displays are well known, and consist of a host
6 material and an activator or dopant. The host material is usually a compound of a Group II
7 element of the periodic table, with a Group VI element, or is a thiogallate compound.
8 Examples of typical phosphors include zinc sulfide or strontium sulfide, with a dopant or
9 activator which functions as the luminescent center when an electric field is applied across
10 the phosphor. Typical activators with phosphors based on zinc sulfide include manganese
11 (Mn) for an amber emission, terbium (Tb) for a green emission and samarium (Sm) for a red
12 emission. A typical activator with phosphors based on strontium sulfide is Ce for a blue-
13 green emission. It is conventional to refer to phosphors as, for example, SrS:Ce to designate
14 a phosphor based on SrS doped with Ce, and ZnS:Mn to designate a phosphor based on ZnS
15 doped with Mn, and this convention is used herein. It is also conventional, when using the
16 formula for the phosphor, for example as in ZnS, to mean phosphors which are formed
17 predominantly from a stoichiometric zinc sulfide. Other elements might be included in the
18 host material for the phosphor, however it is typically still referred to as a phosphor based on
19 the predominant component of the host material. Thus for instance when referring to a
20 phosphor based on zinc sulfide, or a zinc sulfide phosphor, the terminology includes both
21 pure zinc sulfide as a host material and, for example, the phosphor $\text{Zn}_{1-x}\text{Mg}_x\text{S}: \text{Mn}$
22 (designating a phosphor based on zinc sulfide but also including magnesium sulfide in the
23 zinc sulfide host material, doped with Mn), although it is also understood that ZnS and Zn_{1-}
24 $x\text{Mg}_x\text{S}$ are different host materials. This phosphor terminology is used herein and the patent
25 claims.

SUMMARY OF THE INVENTION

26 The present invention provides improvements in a thick film dielectric layer for use in
27 a hybrid thick film/thin film electroluminescent device. The thick film dielectric layer of this
28 invention is formed by thick film techniques from a dielectric material having a high
29 dielectric constant, generally greater than about 500. The improvements are realized by
30 compressing, for example by isostatic pressing, the thick film dielectric layer prior to
31 sintering, to significantly reduce the porosity and the thickness of the layer, and to
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1 significantly increase the dielectric strength of the layer. The result is an unexpected
2 improvement in the dielectric properties of the dielectric layer, significant reductions in the
3 thickness, porosity, void space and interconnectedness of the void space of the layer, and an
4 improvement in the surface smoothness of the layer, leading to more uniform luminance and
5 reduced dielectric breakdown in electroluminescent displays formed therefrom.

6 Electroluminescent laminates made with the thick film dielectric as set forth in U.S.
7 Patent 5,432,015, generally show uniform luminosity as viewed by the naked eye, but when
8 viewed under a X100 microscope show a mottled appearance with some areas brightly
9 illuminated and other areas dimly illuminated or not illuminated at all. When the driving
10 voltage is near the threshold voltage this mottled appearance is most pronounced. The effect
11 is diminished as the voltage is increased above this value and all regions become illuminated.
12 The effect of this behavior is that the onset of luminosity occurs gradually as the voltage is
13 raised above the nominal threshold value and the rate of increase in the average luminosity
14 with increasing voltage is relatively low. The scale of the observed variability of the
15 luminosity is of the order of 10 μm . In contrast, electroluminescent laminates made with a
16 thick film dielectric layer which has been isostatically pressed prior to sintering, in
17 accordance with this invention, do not show this mottled characteristic of the luminosity near
18 the threshold voltage and increases nearly linearly up to about 50 volts above the threshold
19 voltage, so that the average luminosity at a fixed voltage above the threshold voltage is about
20 50% higher than for an otherwise identical electroluminescent laminate. "Uniform
21 luminosity", as used herein, means the luminosity resolved to a scale of about 10 μm appears
22 uniform.

23 Broadly stated, in one aspect of the invention there is provided a method of forming a
24 thick film dielectric layer in an EL laminate of the type including one or more phosphor layers
25 sandwiched between a front and a rear electrode, the phosphor layer being separated from the
26 rear electrode by the thick film dielectric layer, comprising:

27 depositing a ceramic material in one or more layers on a rigid substrate providing the
28 rear electrode, by a thick film technique, to form a dielectric layer having a thickness of 10 to
29 300 μm ;

30 pressing the dielectric layer to form a densified layer with reduced porosity and
31 surface roughness; and

32 sintering the dielectric layer to form a pressed, sintered dielectric layer which, in an

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1 EL laminate, has an improved uniform luminosity over an unpressed, sintered dielectric layer
2 or the same composition.

3 In another broad aspect, the invention provides an improved combined substrate and
4 dielectric layer component for use in an EL laminate, comprising:

5 a rigid substrate providing a rear electrode;

6 a thick film dielectric layer on the substrate providing the rear electrode, the thick film
7 dielectric layer being formed from a pressed, sintered ceramic material having, compared to
8 an unpressed, sintered dielectric layer of the same composition, improved dielectric strength,
9 reduced porosity and uniform luminosity in an EL laminate.

10 In still a further broad aspect, the invention provides an EL laminate, comprising:

11 a planar phosphor layer;

12 a front and rear planar electrode on either side of the phosphor layer;

13 a rear substrate providing the rear electrode, the rear substrate having sufficient
14 mechanical strength and rigidity to support the laminate; and

15 a thick film dielectric layer on the substrate providing the rear electrode, the thick film
16 dielectric layer being formed from a pressed, sintered ceramic material having, compared to an
17 unpressed, sintered dielectric layer of the same composition, improved dielectric strength,
18 reduced porosity and uniform luminosity in an EL laminate.

19 The present invention further provides a patterned phosphor structure particularly
20 useful in AC thin film/thick film electroluminescent devices, and also useful in AC thin film
21 electroluminescent devices if the thickness of the phosphor over the sub-pixels is not too great.
22 In the phosphor structure of the invention, the emitted light from the phosphor underlying the
23 red, green and blue sub-pixels falls within a narrowed wavelength range of the visible
24 electromagnetic spectrum that more closely matches the range transmitted by the respective
25 filters. In this manner, both the luminosity and the energy efficiency of the display can be
26 substantially increased over the values achievable with a conventional colour by white
27 phosphor design. Another feature of the patterned phosphor structure of the present invention
28 is that the sub-pixel threshold voltages can be made equal and, the relative luminosities of the
29 sub-pixels can be set so that they bear set ratios to one another at each operating modulation
30 voltage used to generate the desired luminosities for red, green and blue. Preferably, the set
31 ratios remain substantially constant over the full range of the modulation voltage, for proper
32 colour balance. Most preferably, for a full colour display, the set luminosity ratios for the red,

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1 green and blue sub-pixels are in the ratio of about 3:6:1, or sufficiently close to this ratio so as
2 to enable adequate colour fidelity (gray scale).

3 To reduce the negative impact of the limitations inherent in filter characteristics, it is
4 desirable to use a phosphor for the blue sub-pixels that does not emit significant intensities of
5 green or red light. Cerium doped strontium sulfide (SrS:Ce), optionally codoped with
6 phosphorus, preferably prepared as set out herein, provides desirable CIE colour coordinates
7 and luminosity for the blue, and optionally for the green sub-pixels. For green sub-pixels,
8 manganese doped zinc sulfide (ZnS:Mn) does not generally provide an adequate luminosity
9 when filtered to provide acceptable colour coordinates, but in accordance with this invention,
10 it can be combined with cerium doped strontium sulfide to give higher luminosity with good
11 colour coordinates. Alternatively, $Zn_{1-x}Mg_xS:Mn$, which, with an appropriate ratio of Zn to
12 Mg, has a higher luminosity in the green region of the spectrum than does ZnS:Mn, can be
13 used for the green sub-pixels, optionally with ZnS:Mn. Either or both of the $Zn_{1-x}Mg_xS:Mn$ or
14 the ZnS:Mn phosphors can be used for the red sub-pixels, x being between 0.1 and 0.3.

15 In accordance with this invention, one or more means are included with the one or
16 more of the phosphor deposits for setting and equalizing the threshold voltages of the sub-
17 pixels, and for setting the relative luminosities of the sub-pixels so that they bear set ratios to
18 one another at each operating modulation voltage used to generate the desired luminosities for
19 red, green and blue. Threshold voltage means the highest amplitude of a voltage pulse that,
20 when applied to a sub-pixel at the desired repetition rate, generates a measurable filtered
21 luminosity less than the lowest specified gray scale luminosity for that sub-pixel. Thus, the
22 means for setting and equalizing the threshold voltages also functions to set the relative sub-
23 pixel luminosities so that they bear set ratios to one another over the full range of the
24 modulation voltage used. Generally, the means is one or more of (a) a threshold voltage
25 adjustment layer formed from a dielectric or semiconductor material which is located in one or
26 more of the positions of over, under and embedded within one or more of the phosphor
27 deposits, and/or (b) one or more of the phosphor deposits being formed with different
28 thicknesses.

29 It should be noted that the terms "sub-pixel" and "sub-pixel phosphor elements" are
30 used interchangeably herein to refer to the phosphor deposits for a particular red, green or blue
31 sub-pixel element, along with any threshold voltage adjustment deposit associated with that
32 sub-pixel element.

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Appropriate colour filters can be chosen for the three sub-pixels to achieve self-consistent optimization of luminosity and colour coordinates for each, and overall pixel energy efficiency. The present invention has application to other colour phosphors, the strontium sulfide and zinc sulfide phosphors being representative only. Usually, at least two different phosphors are used, each being formed from different host materials. It is also possible to extend the present invention to three or more different phosphor layers for further optimization.

Broadly stated, the invention provides a patterned phosphor structure having red, green and blue sub-pixel phosphor elements for an AC electroluminescent display, comprising:

at least a first and a second phosphor, each emitting light in different ranges of the visible spectrum, but whose combined emission spectra contains red, green and blue light;

said at least first and second phosphors being in a layer, arranged in adjacent, repeating relationship to each other to provide a plurality of repeating at least first and second phosphor deposits; and

one or more means associated with one or more of the at least first and second phosphor deposits, and which together with the at least first and second phosphor deposits, form the red, green and blue sub-pixel phosphor elements, for setting and equalizing the threshold voltages of the red, green and blue sub-pixel phosphor elements, and for setting the relative luminosities of the red, green and blue sub-pixel phosphor elements so that they bear set ratios to one another at each operating modulation voltage used to generate the desired luminosities for red, green and blue.

Suitable materials for the threshold voltage adjustment layers are those which, when deposited as a layer, at an appropriate thickness, will not conduct until the voltage across the patterned phosphor structure exceeds the threshold voltage for an otherwise identical patterned phosphor structure that does not include the threshold voltage adjustment layer. A suitable material can be chosen by examination of its dielectric constant and dielectric breakdown strength to meet the above condition, with materials having relatively high dielectric constants and dielectric breakdown strengths as compared to those of the phosphor materials being preferable. The materials for the threshold voltage adjustment layer are compatible with those materials that are in contact with them in the patterned phosphor structure, and are chosen from dielectric materials and semiconductors. By semiconductors is meant both intrinsic semiconductors, and semiconductors with deep impurity levels that have effective electronic

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band gaps that are comparable to, or larger than, the effective band gap of the phosphor material. Examples of suitable materials include binary metal oxides such as alumina and tantalum oxide, binary metal sulfides such as zinc sulfide and strontium sulfide, silica, and silicon oxynitride. The suitability of these materials is dependent on the properties of the interface between the materials and any phosphor materials and the dielectric materials in contact with them. In general, when the phosphor deposit is of a phosphor which is based on zinc sulfide, the preferred threshold voltage adjustment material is a binary metal oxide, most preferably alumina.

Alternatively, or in addition, the means for setting and equalizing the threshold voltages and for setting the relative luminosities comprises forming the first and second phosphor deposits with different thicknesses so as to balance the threshold voltages and the luminosities of the sub-pixel elements. In this case, the overall colour balance can be achieved for a pixel by setting the luminosities for the sub-pixel by using different sub-pixel element areas, for instance by making the sub-pixel elements of the less efficient phosphors wider than the width of the sub-pixel elements with the more efficient phosphors.

The patterned phosphor structure of this invention allows for correct CIE colour coordinates for a full colour display to be achieved for all operating modulation voltage levels, while allowing for the equalizing of the threshold voltages of the sub-pixel elements. The means for setting and equalizing the threshold voltages, and for setting the relative luminosities of the red, green and blue sub-pixels may also comprise, in addition to the threshold voltage adjustment deposits and/or altering the thicknesses of the phosphor deposits, varying one or more of the following in order to set the relative luminosities:

- 23 i. the areas of the phosphor deposits; and
- 24 ii. the concentrations of a dopant or co-dopant in the phosphor deposits.

Preferably, the first and second phosphors are of different host materials, such as a strontium sulfide phosphor or a zinc sulfide phosphor. Generally, a different host material implies that a different element has been introduced to the phosphor host material at an atomic percent greater than about 5 atomic percent. Preferred first and second phosphors are SrS:Ce and ZnS:Mn; SrS:Ce and $Zn_{1-x}Mg_xS:Mn$; or SrS:Ce with layers of both ZnS:Mn and $Zn_{1-x}Mg_xS:Mn$, it being possible for the SrS:Ce to be codoped with phosphorus. These are examples of zinc sulfide and strontium sulfide phosphors which, if they were superimposed, would have a combined emission spectrum which covers the wavelengths of white light

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(individual visible spectra for ZnS:Mn and SrS:Ce are shown in Figures 7 and 8 respectively). Within the scope of the present invention, each of the first and second phosphor deposits may comprise one or more layers of a same or different phosphor for each sub-pixel element, and each of the phosphor deposits may themselves be composed of one or more phosphor compositions (i.e. mixtures of more than one phosphors). As set out below, the phosphor structure of this invention may be provided on one or more layers. For example, in a single layer phosphor structure, as set forth in Example 3, the phosphors can be arranged such that $Zn_{1-x}Mg_xS:Mn$ forms the red and green sub-pixel elements, while SrS:Ce forms the blue sub-pixel element. A threshold voltage adjustment layer of a binary metal oxide such as alumina can be provided over the red and green sub-pixel elements to achieve the desired luminous intensity ratios between the sub-pixel elements. Alternatively, as set forth in Example 4, SrS:Ce deposits can be used for the blue sub-pixel elements, and a layer of $Zn_{1-x}Mg_xS:Mn$ between layers of ZnS:Mn can be used for the red and green sub-pixel elements. The stacked zinc sulfide phosphor deposits of this embodiment can be formed thick enough to equalize the threshold voltages between the sub-pixel elements. To achieve the desired relative luminosities between the sub-pixel elements, the SrS:Ce deposits for the blue sub-pixels can be made wider than the sub-pixels for red and green. Alternatively, as set forth in Example 5, SrS:Ce deposits can be used for both the green and blue sub-pixel elements, and ZnS:Mn can be used for the red sub-pixel elements. A threshold voltage adjustment layer of a binary metal oxide such as alumina can be used over the red sub-pixel deposits to equalize the threshold voltages.

When two layers of phosphors are used, as in Example 2, the phosphors may be arranged such that SrS:Ce is patterned in a first layer with ZnS:Mn or $Zn_{1-x}Mg_xS:Mn$, and a second layer of SrS:Ce can be formed over the first layer. In this embodiment, the stacked phosphor deposits of SrS:Ce form the blue sub-pixel elements, while the red and green sub-pixel elements are formed by the stacked zinc sulfide phosphor deposit under the SrS:Ce deposit.

Compared to conventional colour by white techniques in which the white light is provided by coplanar, stacked layers of SrS:Ce and ZnS:Mn, the patterned phosphor structure of the present invention has the advantage of being able to provide a thicker layer of SrS:Ce for the blue sub-pixel element, without having an over- or under- layer of ZnS:Mn. This results in increased blue luminance and, since there is no yellow-orange light being emitted in

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1 the blue sub-pixels, the filtered light from the SrS:Ce phosphor is a more saturated blue.

2 The patterned phosphor structure of this invention has particular application in hybrid
3 thick film/thin film AC electroluminescent devices such as described in U.S. Patent 5,432,015,
4 in which the EL laminate is fabricated on a rigid rear substrate, with a thick film dielectric
5 layer below the phosphor structure. AC thin film electroluminescent devices (TFELs) have
6 the disadvantage of generally requiring its thin layers to be planarized, that is of even
7 thicknesses. Such devices generally preclude the ability to use colour phosphor sub-pixels of
8 differing thicknesses. However, using a thick film dielectric layer in an EL laminate in
9 combination with the patterned phosphor structure of the present invention allows one to use
10 different thicknesses of the individual phosphor sub-pixel deposits, so as to optimize the
11 colour coordinates and luminosity of a particular sub-pixel element, while still setting and
12 equalizing the threshold voltages for the sub-pixel elements.

13 The present invention also extends to novel methods for fabricating the patterned
14 phosphor structure of the present invention. Broadly stated, the invention provides a method
15 of forming a patterned phosphor structure having red, green and blue sub-pixel elements for an
16 AC electroluminescent display, comprising:

17 selecting at least a first and a second phosphor, each emitting light in different ranges
18 of the visible spectrum, but whose combined emission spectra contains red, green and blue
19 light;

20 depositing and patterning said at least first and second phosphors in a layer to form a
21 plurality of repeating at least first and second phosphor deposits arranged in adjacent,
22 repeating relationship to each other; and

23 providing one or more means associated with one or more of the at least first and
24 second phosphor deposits, and which together with the at least first and second phosphor
25 deposits, form the red, green and blue sub-pixel phosphor elements, for setting and equalizing
26 the threshold voltages of the red, green and blue sub-pixel phosphor elements, and for setting
27 the luminosities of the red, green and blue sub-pixel elements so that they bear set relative
28 luminosities to one another at each operating modulation voltage used to generate the desired
29 luminosities for red, green and blue; and

30 optionally annealing the patterned phosphor structure so formed.

31 Preferably the patterning of the at least first and second phosphor is achieved by
32 photolithographic techniques, including the steps of:

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- 1 a) depositing a layer of the first phosphor which is to form at least one of the red, green
2 and blue sub-pixel elements;
- 3 b) removing the first phosphor material in regions which are to define the other of the
4 red, green and blue sub-pixel elements, leaving spaced first phosphor deposits;
- 5 c) depositing the second phosphor over the first phosphor deposits and in the regions
6 which are to define the other of the red, green and blue sub-pixel elements; and
- 7 d) removing the second phosphor from above the first phosphor deposits, leaving a
8 plurality of repeating first and second phosphor deposits arranged in adjacent, repeating
9 relationship to each other.

10 Novel photolithographic techniques have been developed which are particularly useful
11 in patterning strontium and zinc sulfide phosphors, but which have application to other
12 phosphor combinations. In its most preferred embodiments, the photolithographic methods of
13 this invention utilizes a negative photoresist, and has the advantage of needing only one photo-
14 mask to accomplish the patterning of the red, green and blue sub-pixel elements. In
15 accordance with this method, steps b) through d) include, applying a negative resist to the
16 first phosphor; exposing and developing the resist through a photo-mask in the areas that the
17 first phosphor is to define one or more of the red, green and blue sub-pixel elements; removing
18 the first phosphor as in step b), depositing the second phosphor over the first phosphor
19 deposits and in the regions which are to define the other of the red, green and blue sub-pixel
20 elements; and then removing, by lift-off, the second phosphor from above the first phosphor
21 deposits. Typically in this method, the first phosphor is a strontium sulfide phosphor, most
22 preferably SrS:Ce, which forms the blue sub-pixel elements and optionally the green sub-pixel
23 elements, and the second phosphor is a zinc sulfide phosphor, most preferably ZnS:Mn or Zn_{1-x}Mg_xS:Mn, or both, which forms the red, and optionally the green, sub-pixel elements. In
24 accordance with the method, the means for setting and equalizing the threshold voltages and
25 for setting the luminosities of the sub-pixel elements can include adding a threshold voltage
26 adjustment deposit beneath, within or above one or more of the phosphor deposits and/or
27 forming the phosphor deposits with different thicknesses, as set out above. In addition, the
28 means for setting and equalizing the threshold voltages, and for setting the luminosities, of the
29 sub-pixel elements may include varying one or more of:

- 31 i. the areas of the phosphor deposits; and
- 32 ii. the concentrations of a dopant or co-dopant in the phosphor deposits.

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1 The invention also provides a novel photolithographic technique which is particularly
2 useful for patterning a phosphor which is subject to hydrolysis, such as alkaline earth metal
3 sulfide or selenide phosphors. Broadly, the invention provides a method of forming a
4 patterned phosphor structure having red, green and blue sub-pixel elements for an AC
5 electroluminescent display, comprising:

6 a) selecting at least a first and a second phosphor, each emitting light in different
7 ranges of the visible spectrum, but whose combined emission spectra contains red, green and
8 blue light;

9 b) depositing a layer of the first phosphor which is to form at least one of the red, green
10 or blue sub-pixel elements;

11 c) applying a photo-resist to the first phosphor, exposing the photo-resist through a
12 photo-mask, developing the photo-resist, and removing the first phosphor in regions that the
13 first phosphor is to define as one or more of the red, green and blue sub-pixel elements,
14 leaving spaced first phosphor deposits, wherein the first phosphor is removed with an etchant
15 solution comprising a mineral acid, or a source of anions of a mineral acid, in a non-aqueous,
16 polar, organic solvent which solubilizes the reaction product of the first phosphor with anions
17 of the mineral acid, and wherein optionally, prior to removing the first phosphor with the
18 etchant solution, the first phosphor layer is immersed in the non-aqueous organic solvent;

19 d) depositing the second phosphor material over the first phosphor deposits and in
20 regions which are to define the other of the red, green and blue sub-pixel elements; and

21 e) removing by lift-off, the second phosphor material and the resist from above the first
22 phosphor deposits leaving a plurality of repeating first and second phosphor deposits arranged
23 in adjacent, repeating relationship to each other.

24 The invention also extends to EL laminates combining, as described above, a rigid rear
25 substrate, a thick film dielectric layer and the patterned phosphor structure, together with front
26 and rear column and row electrodes on either side of the phosphor layer, in which the front and
27 rear column and row electrodes are generally aligned with the phosphor sub-pixel elements,
28 and bandpass colour filter means aligned with the red, green and blue phosphor sub-pixel
29 elements for passing therethrough red, green and blue light emitted from the phosphor sub-
30 pixel elements.

31 Another aspect of the present invention provides novel and separate selection criteria
32 for barrier diffusion layers and injection layers useful with electroluminescent phosphors, and

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1 particularly useful with the patterned phosphor structure and the thick film dielectric of the
2 present invention. Preferably, a diffusion barrier layer is included above the thick film
3 dielectric layer, or if present, above the second ceramic material. The diffusion barrier layer is
4 composed of a metal-containing electrically insulating binary compound which is compatible
5 with any adjacent layers, and which is precisely stoichiometric, preferably varying from its
6 precise stoichiometric composition by less than 0.1 atomic percent, and having a thickness of
7 100 to 1000 Å. Preferred materials will vary with the particular phosphors and the materials in
8 the dielectric layers, but most preferred materials are alumina, silica and zinc sulfide.
9 Preferably, an injection layer is included above the thick film dielectric layer, or if present,
10 above the second ceramic material or the barrier diffusion layer, to provide a phosphor
11 interface. The injection layer is composed of a binary dielectric or semi-conductor material
12 which is non-stoichiometric in its composition and which has electrons in a preferred range of
13 energy for injection into the phosphor layer. The material is compatible with adjacent layers
14 and is preferably non-stoichiometric by greater than 0.5 atomic percent. Preferred materials
15 vary with the particular phosphor and the materials in the underlying dielectric layers, but
16 preferred materials for providing optimum electron energies are hafnia or yttria. There is a
17 compromise between optimum electron injection and compatibility with adjacent layers. As a
18 result, sometimes a non-stoichiometric compound cannot be used as an injection layer.

19 Another broad aspect of the invention provides a method of synthesizing strontium
20 sulfide, comprising:

21 providing a source of high purity strontium carbonate in a dispersed form;
22 heating the strontium carbonate in a reactor with gradual heating up to a maximum
23 temperature in the range of 800 to 1200°C;
24 contacting the heated strontium carbonate with a flow of sulfur vapours formed heating
25 elemental sulfur in the reactor to at least 300°C in an inert atmosphere; and
26 terminating the reaction by stopping the flow of sulfur at a point when sulfur dioxide or
27 carbon dioxide in the reaction gas reaches an amount which correlates with an amount of
28 oxygen in oxygen-containing strontium compounds in the reaction product which is in the
29 range of 1 to 10 atomic percent.

30 By "dispersed form", in reference to the source of strontium carbonate, as used herein
31 and in the claims, is meant that the strontium carbonate powder particles are exposed to the
32 process conditions substantially uniformly. This can preferably be achieved by using small

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1 batches, using volatile, non-contaminating, clean evaporating compounds or solvents which
2 decompose into gaseous products prior to the onset of the reaction, using fluidized beds or
3 tumbler reactors.

4 The term "phosphor" as used herein and in the claims, means a substance which
5 provides electroluminescence when a sufficient electric field is applied across it, and electrons
6 are injected into it.

7 The term "white light" when used herein and in the claims, when referring to the
8 combined emission spectra of two or more phosphors, means that white light is emitted when
9 the phosphors are superimposed in a manner such that the light can be filtered to provide red,
10 green and blue light.

11 The term "compatible" when used herein and in the claims, means that the material is
12 chemically stable to that it does not chemically react with adjacent layers.

BRIEF DESCRIPTION OF THE DRAWINGS

14 Figure 1 is a schematic sectional view of an EL laminate having a thick film dielectric
15 of the present invention with conventional colour by white bilayer phosphors and red, green
16 and blue filters;

17 Figure 2 is a schematic sectional view of an EL laminate having a thick film dielectric
18 of the present invention combined with a two layer patterned phosphor structure of the present
19 invention;

20 Figure 3 is a graph comparing the unfiltered luminance plotted against voltage for the
21 colour by white structure of Figure 1 (shown in dotted line in the graph) and the patterned
22 phosphor structure of Figure 2 (shown in solid lines in the graph), at a driving frequency of 60
23 Hz;

24 Figure 4 is a graph comparing the filtered luminances plotted against voltage for the
25 colour by white structure of Figure 1 and the patterned phosphor structure of Figure 2, at a
26 driving frequency of 60 Hz:

27 Figure 5 is a plan view of the ITO column electrode over several pixels, showing
28 alignment with the underlying red, green and blue phosphor sub-pixel elements;

29 Figure 6 is a schematic sectional view of a single pixel of an EL laminate with a two
30 layer patterned phosphor structure of the present invention with additional diffusion barrier
31 and injection layers;

32 Figure 7 is a graph of the emission spectrum for ZnS:Mn, plotting intensity in arbitrary

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1 units against wavelength in nanometres;

2 Figure 8 is a graph of the emission spectrum for SrS:Ce, when synthesized by the
3 process of the present invention, plotting intensity in arbitrary units against wavelength in
4 nanometres; and

5 Figure 9 is a schematic plot of energy against distance to illustrate phosphor electron
6 bands in the presence of an electric field.

7 The figures showing the thick film dielectric layers and the patterned phosphor
8 structures of this invention are not shown to scale.

9 DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 EL Laminate With Isostatic Pressed Thick Film Dielectric

11 The present invention provides a thick film dielectric layer having increased dielectric
12 strength and dielectric constant, significantly reduced void space, void interconnectedness,
13 porosity and thickness, and significantly improved surface smoothness, when compared to the
14 thick films dielectric layers such as described in U.S. Patent 5,432,015. The smoother surface
15 of the dielectric layer results in an unexpected improvement by providing a higher and more
16 uniform luminosity across an EL display formed therefrom. The improvement is achieved by
17 compressing a thick film dielectric layer prior to sintering, such as by isostatic pressing.

18 The thick film dielectric layer will be described with reference to Figures 1, 2, 5 and 6.
19 An EL laminate 10 is built from the rear to the front (viewing) side on a rear substrate 12.
20 Preferably, the substrate 12 is a rigid substrate such as a preformed sheet, providing sufficient
21 mechanical strength and rigidity to support the laminate 10. Alternatively, the substrate 12
22 could be a green tape or the like which will sinter to provide the rigidity for the laminate 10.
23 Thus, the term "rigid substrate" as used herein refers to the substrate after sintering. The
24 substrate 12 is preferably formed from a ceramic which can withstand the high sintering
25 temperatures (typically up to 1000°C) used in processing other layers of the laminate 10. An
26 alumina sheet is most preferred, having a thickness and rigidity sufficient to support the EL
27 laminate 10. A rear electrode layer 14 is formed on the substrate 12. For lamp applications,
28 the rear substrate 12 and rear electrode 14 might be integral, for example by being provided by
29 a rigid, electrically conductive metal sheet. For display applications, the rear electrode 14
30 consists of rows of conductive metal address lines centered on the substrate 12 and spaced
31 from the substrate edges. Preferably conductive metal address lines are screen printed from
32 noble metal pastes, as is well known. An electrical contact tab 16 protrudes from the electrode

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1 14, as seen in Figure 5. The thick film dielectric layer 18 is formed above the electrode 14,
2 and may be formed as a single layer, or as multiple layers. In Figures 1 and 2, the layer is
3 shown schematically as one layer, while in Figure 6, the layer comprises a thicker, first
4 dielectric layer 18, and a thinner, second dielectric layer 20. One or more phosphor layers 22
5 are provided above the dielectric layer 18, or dielectric layers 18, 20. In Figure 1, the
6 phosphor is shown as two layers as in a conventional colour by white design. In Figure 2 and
7 6, the phosphor layer 22 is shown to comprise a patterned phosphor structure 30 of the present
8 invention, as is described in greater detail below. Above the phosphor layer(s) 22, there may
9 be provided a third dielectric layer 23. Above the optional third dielectric layer 23 is a front,
10 transparent electrode layer 24. The front electrode layer 24 is shown in Figures 1 and 2 as
11 solid, but in actuality, for display applications, it consists of columns of address lines arranged
12 perpendicularly to the row address lines of the rear electrode 14. The front electrode 24 is
13 preferably formed from indium tin oxide (ITO) by known thin film or photolithographic
14 techniques. Although not shown, the front electrode is also provided with an electrical contact.
15 Figures 1 and 2 show bandpass colour filter means 25 above the ITO lines, such as polymeric
16 red, green and blue filters 25a, 25b, and 25c respectively, aligned with the ITO address lines.
17 In Figure 2, these filters 25a, 25b, and 25c are also aligned with red, green and blue phosphor
18 sub-pixel elements 30a, 30b and 30c, in the patterned phosphor structure 30. Also not shown,
19 the EL laminate 10 is encapsulated with a transparent sealing layer to prevent moisture
20 penetration. The EL laminate 10 is operated by connecting an AC power source to the
21 electrode contacts. Voltage driving circuitry (not shown) is well known in the art. The EL
22 laminate 10, incorporating the thick film dielectric layer 18, has application in both EL lamps
23 and displays.

24 It will be understood by persons skilled in the art that further intervening layers,
25 including for example one or more barrier diffusion layers 26, injection layers 28 or dielectric
26 layers (such as optional second and third dielectric layers 20, 23, respectively) can be included
27 in the laminate 10, some of which are described more particularly below in association with
28 the patterned phosphor structure 30. Thus, throughout this description and in the patent
29 claims, when an EL laminate is defined as including certain layers, additional, intervening
30 layers are not meant to be excluded.

31 It will be appreciated that, in general, the criteria for establishing the thickness and
32 dielectric constant of the dielectric layer(s) are calculated so as to provide adequate dielectric

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1 strength at minimal operating voltages. The criteria are interrelated as set forth below, in
2 respect of a single phosphor layer and a single dielectric layer. In the case of multilayers, such
3 as a two layer phosphor, or the patterned phosphor structure described below, the criteria are
4 adjusted for the multiple layers, for example by using the thickest dimension and average
5 dielectric constant of the entire phosphor layer.

6 Given a typical range of thickness for the phosphor layer (d_1) of between about 0.2 and
7 2.5 microns, a dielectric constant range for the phosphor layer (k_1) of between about 5 and 10
8 and a dielectric strength range for the dielectric layer(s) of about 10^6 to 10^7 V/m, the following
9 relationships and calculations can be used to determine typical thickness (d_2) and dielectric
10 constant (k_2) values for the dielectric layer of the present invention. These relationships and
11 calculations may be used as guidelines to determine d_2 and k_2 values, without departing from
12 the intended scope of the present invention, should the typical ranges change significantly.

13 The applied voltage V across a bilayer comprising a uniform dielectric layer and a
14 uniform non-conducting phosphor layer sandwiched between two conductive electrodes is
15 given by equation 1:

16
$$V = E_2 * d_2 + E_1 * d_1 \quad (1)$$

17 wherein:

18 E_2 is the electric field strength in the dielectric layer;

19 E_1 is the electric field strength in the phosphor layer;

20 d_2 is the thickness of the dielectric layer; and

21 d_1 is the thickness of the phosphor.

22 In these calculations, the electric field direction is perpendicular to the interface
23 between the phosphor layer and the dielectric layer. Equation 1 holds true for applied voltages
24 below the threshold voltage at which the electric field strength in the phosphor layer is
25 sufficiently high that the phosphor begins to break down electrically and the device begins to
26 emit light.

27 From electromagnetic theory, the component of electric displacement D perpendicular
28 to an interface between two insulating materials with different dielectric constants is
29 continuous across the interface. This electric displacement component in a material is defined
30 as the product of the dielectric constant and the electric field component in the same direction.
31 From this relationship equation 2 is derived for the interface in the bilayer structure:

32
$$k_2 * E_2 = k_1 * E_1 \quad (2)$$

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wherein:

k_2 is the dielectric constant of the dielectric material; and
 k_1 is the dielectric constant of the phosphor material.

Equations 1 and 2 can be combined to give equation 3:

$$V = (k_1 * d_2 / k_2 + d_1) * E_1 \quad (3)$$

To minimize the threshold voltage, the first term in equation 3 needs to be as small as is practical. The second term is fixed by the requirement to choose the phosphor thickness to maximize the phosphor light output. For this evaluation the first term is taken to be one tenth the magnitude of the second term. Substituting this condition into equation 3 yields equation 4:

$$d_2/k_2 = 0.1 * d_1/k_1 \quad (4)$$

Equation 4 establishes the ratio of the thickness of the dielectric layer to its dielectric constant in terms of the phosphor properties. This thickness is determined independently from the requirement that the dielectric strength of the layer be sufficient to hold the entire applied voltage when the phosphor layer becomes conductive above the threshold voltage. The thickness is calculated using equation 5:

$$d_2 = V/S \quad (5)$$

wherein:

S is the strength of the dielectric material.

Use of the above equations and reasonable values for d_1 , k_1 , and S provides the range of dielectric layer thickness and dielectric constant. In general, the lower limit of the thickness of the dielectric layer is that it must be sufficiently thick that the dielectric strength of the dielectric layer is higher than the actual electric field present during operation of the device. Generally, the combined thickness of the dielectric layers 18 and 20 can be as low as about 10 μm , with a phosphor layer thicknesses as high as about 2.5 μm .

A method of constructing the thick film dielectric layer 18 will now be described with preferred materials and process steps.

The dielectric layer 18 is deposited by thick film techniques which are well known in the electronics/semiconductor industries. The layer 18 is preferably formed from a ferroelectric material, most preferably one having a perovskite crystal structure, to provide a high dielectric constant compared to that of the phosphor layer(s) 22. The material will have a minimum dielectric constant of 500 over a reasonable operating temperature for the laminate

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<p>(54) Title: ELECTROLUMINESCENT LAMINATE WITH PATTERNED PHOSPHOR STRUCTURE AND THICK FILM DIELECTRIC WITH IMPROVED DIELECTRIC PROPERTIES</p> <p>(57) Abstract</p> <p>A patterned phosphor structure, and EL laminate containing same (10), forming red, green and blue sub-pixel phosphor elements (30) for an AC electroluminescent display. The patterned phosphor structure includes at least a first (30) and a second phosphor (22) emitting light in different ranges of the visible spectrum, but with combined emission spectra contains red, green and blue light, the first (30) and second phosphors (22) being in a layer, arranged in adjacent, repeating relationship to each other to provide a plurality of repeating first and second phosphor deposits. The phosphor structure also includes one or more means (25) associated with one or more of the first and second phosphor deposits, and which together with the first and second phosphor deposits, form the red (30a), green (30c) and blue (30b) sub-pixel phosphor elements, for setting and equalizing the threshold voltages, and for setting the relative luminosities. Also provided is an improved dielectric layer (16) for use in an EL laminate.</p>			
<p>The diagram illustrates the cross-section of an electroluminescent (EL) laminate. It shows a stack of layers labeled from top to bottom: 10 (the overall laminate), 24, 26, 22, 18, 14, and 12. Layer 22 contains three sub-pixel phosphor elements labeled 30a, 30b, and 30a. Layer 30 is shown on the left side, with an arrow pointing to it from the label '30'. The labels 25C, 25a, 25b, 25C, and 25a are positioned above the top edge of the stack, corresponding to the phosphor structures.</p>			

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1 **ELECTROLUMINESCENT LAMINATE WITH PATTERNED PHOSPHOR**
2 **STRUCTURE AND THICK FILM DIELECTRIC WITH IMPROVED**
3 **DIELECTRIC PROPERTIES**

5 **FIELD OF THE INVENTION**

6 This invention relates to AC electroluminescent (EL) devices fabricated using thin
7 film and/or thick film technologies. The invention also relates to full colour EL devices.

8 **BACKGROUND OF THE INVENTION**

9 U.S. Patent 5,432,015, issued July 11, 1995, to Wu et al., and U.S. Patent 5,756,147,
10 issued May 26, 1998, to Wu et al. disclose an electroluminescent laminate structure which
11 combines a thick film dielectric layer with thin film layers, and a rear to front method of
12 forming same on a rigid, rear substrate. Solid state displays (SSD) using this hybrid thick
13 film/thin film technology have been demonstrated to have good performance and brightness
14 (luminosity) in monochrome (ZnS:Mn phosphor) and full colour (ZnS:Mn/SrS:Ce bilayer
15 phosphor) applications (Bailey et al., SID 95 Digest, 1995), however, improvements are still
16 needed.

17 The potential for EL as a competitive alternative for fabricating flat panel displays has
18 been hindered by the inability to generate bright, stable full colour. This has resulted in EL
19 only penetrating markets for niche applications, in which the inherent benefits of the
20 technology, such as ruggedness, wide viewing angle, temperature insensitivity, and fast time
21 response, are needed.

22 Two basic alternatives have been used to produce full colour EL devices. One
23 approach is to use patterned phosphors, that is alternating red, green and blue (RGB)
24 phosphor elements in a layer (see for example U.S. Patent 4,977,350, issued December 11,
25 1990, to Tanaka et al.). This approach has the disadvantage of requiring the three phosphors
26 to be patterned into red, green and blue sub-pixels that make up each pixel, in separate steps.
27 Furthermore, the three colours cannot all be produced brightly enough by currently available
28 EL phosphors to gain the brightness advantage desired. A second approach is to use a colour
29 by white technique, first described by Tanaka et al., (SID 88 Digest, p 293, 1988, see also,
30 U.S. Patent 4,727,003, issued February 23, 1988 to Ohseto et al.). In the colour by white
31 method, the phosphor layer comprises layers of phosphors, typically ZnS:Mn and SrS:Ce,
32 which when superimposed produce white light. Red, green and blue sub-pixels are then

1 obtained by placing a patterned filter in front of the white light. The white phosphor emits
2 light at wavelengths over the entire visible portion of the electromagnetic spectrum, and the
3 filters transmit a narrowed range of wavelengths corresponding to the colours for each sub-
4 pixel. This approach has the disadvantage of relatively poor energy efficiency, in high
5 measure because a high fraction of the light is absorbed in the filters and the overall energy
6 efficiency of the display is correspondingly reduced.

7 Another requirement for full colour displays is gray scale capability, that is the ability
8 to generate a number of defined and consistent luminosities (light emission intensities) for
9 each sub-pixel. Typically, 256 gray scale luminosities span a range from zero to full
10 luminosity controlled by predetermined input electrical signals for each sub-pixel. This
11 number of gray levels provides a total of about 16 million individual colours.

12 Electroluminescent displays have pixels and sub-pixels that are defined by
13 intersecting sets of conductor stripes at right angles to one another on opposite sides of a
14 phosphor layer. These sets of stripes are respectively referred to as "rows" and "columns".
15 The sub-pixels are independently illuminated using an addressing scheme called passive
16 matrix addressing. This entails sequentially addressing the rows by applying a short flat-
17 topped electrical pulse with a peak voltage called the threshold voltage sequentially on each
18 of the rows such that the duration of the pulse is less than the time allocated for addressing
19 each row. Electrical pulses, each with a defined and independent peak voltage, termed the
20 "modulation voltage", are simultaneously applied to each of the columns intersecting the
21 addressed row. This provides independently controllable voltages across the sub-pixels
22 making up the pixels along that row, in accordance with the instantaneous luminosity
23 required for each sub-pixel to achieve the desired pixel colours. While each row is being
24 addressed, the remaining rows are disconnected, or are connected to a voltage level near zero.
25 Independent operation of all sub-pixels on the display requires that sub-pixels not on the
26 addressed row do not illuminate. The electro-optical characteristics of the sub-pixels on an
27 electroluminescent display facilitate meeting this requirement, by virtue of the fact that no
28 luminosity is generated if the voltage across the sub-pixels is below the threshold voltage.

29 The time required to address all the rows in a display is called a frame, and for video
30 images, the frame repetition rate must be at least about 50 Hz in order to avoid image flicker.
31 At the same time there is a maximum frame repetition rate, typically about 200 Hz, that is

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1 achievable due to a limitation on the voltage rise time associated with the electrical
2 characteristics of the display and its associated electronics. In principle, a measure of gray
3 scale can be achieved by controlling the average pixel luminosity by modulating the average
4 frame rate. This requires omitting a fraction of the electrical pulses over a suitably short
5 period of time. In practice, however, due to the limited range of frame rates, only a few levels
6 of gray scale can be realized this way. Another option, called dithering, is to extinguish one
7 or more pixels in the immediate vicinity of a pixel where reduced luminosity is required,
8 thereby spatially modulating luminosity. This technique, however, causes a loss of display
9 resolution and image quality.

10 The preferred method of gray scale control is to control the instantaneous sub-pixel
11 luminosity, which must be done by modulating the electrical pulse peak voltage, pulse
12 duration or pulse shape. At the same time, to minimize power consumption in
13 electroluminescent displays addressed using passive matrix addressing, it is desirable to have
14 the row voltage as close as possible to the threshold voltage above which luminosity is
15 generated. This requires the threshold voltage for all sub-pixels to be equal.

16 Filters used to tailor the spectral emission characteristics of sub-pixels typically do not
17 have ideal characteristics. They do not have perfect transmission in the desired wavelength
18 ranges to achieve the desired red, green and blue colours, and they have some optical
19 transparency in the wavelength ranges where they should be opaque. These deviations from
20 ideal behavior impose design limitations on the overall pixel design. For example, the
21 polymer based blue filters commonly used for electroluminescent and other types of flat panel
22 displays have some transmission also in the red portion of the spectrum. The need to
23 suppress red contamination of the blue pixel requires that thicker polymer films be used,
24 which reduces the transparency in the desired blue wavelength range. They also have some
25 transparency in the green wavelength range introducing a similar requirement for thicker
26 polymers that are less transparent to blue light. To meet the requirements for full colour
27 displays, the ratios of luminosity for red:green:blue sub-pixels should be 3:6:1, to give a
28 white colour for that pixel. The CIE colour coordinates for red sub-pixels should be in the
29 range $0.60 < x < 0.65$ and $0.34 < y < 0.36$. The CIE colour coordinates for green sub-pixels should
30 be in the range $0.35 < x < 0.38$ and $0.55 < y < 0.62$. For blue sub-pixels the CIE colour
31 coordinates should be in the range $0.13 < x < 0.15$ and $0.14 < y < 0.18$. The combined (white)

1 luminosity for a pixel comprising red, green and blue sub-pixels should be at least about 70
2 candelas per square meter (cd/m^2) and the CIE colour coordinates for full white should be in
3 the range $0.35 < x < 0.40$ and $0.35 < y < 0.40$. Higher luminosity is desirable for some
4 applications.

5 Phosphors useful in electroluminescent displays are well known, and consist of a host
6 material and an activator or dopant. The host material is usually a compound of a Group II
7 element of the periodic table, with a Group VI element, or is a thiogallate compound.
8 Examples of typical phosphors include zinc sulfide or strontium sulfide, with a dopant or
9 activator which functions as the luminescent center when an electric field is applied across
10 the phosphor. Typical activators with phosphors based on zinc sulfide include manganese
11 (Mn) for an amber emission, terbium (Tb) for a green emission and samarium (Sm) for a red
12 emission. A typical activator with phosphors based on strontium sulfide is Ce for a blue-
13 green emission. It is conventional to refer to phosphors as, for example, SrS:Ce to designate
14 a phosphor based on SrS doped with Ce, and ZnS:Mn to designate a phosphor based on ZnS
15 doped with Mn, and this convention is used herein. It is also conventional, when using the
16 formula for the phosphor, for example as in ZnS , to mean phosphors which are formed
17 predominantly from a stoichiometric zinc sulfide. Other elements might be included in the
18 host material for the phosphor, however it is typically still referred to as a phosphor based on
19 the predominant component of the host material. Thus for instance when referring to a
20 phosphor based on zinc sulfide, or a zinc sulfide phosphor, the terminology includes both
21 pure zinc sulfide as a host material and, for example, the phosphor $\text{Zn}_{1-x}\text{Mg}_x\text{S:Mn}$
22 (designating a phosphor based on zinc sulfide but also including magnesium sulfide in the
23 zinc sulfide host material, doped with Mn), although it is also understood that ZnS and $\text{Zn}_{1-
24 x}\text{Mg}_x\text{S}$ are different host materials. This phosphor terminology is used herein and the patent
25 claims.

26 SUMMARY OF THE INVENTION

27 The present invention provides improvements in a thick film dielectric layer for use in
28 a hybrid thick film/thin film electroluminescent device. The thick film dielectric layer of this
29 invention is formed by thick film techniques from a dielectric material having a high
30 dielectric constant, generally greater than about 500. The improvements are realized by
31 compressing, for example by isostatic pressing, the thick film dielectric layer prior to
32 sintering, to significantly reduce the porosity and the thickness of the layer, and to

1 significantly increase the dielectric strength of the layer. The result is an unexpected
2 improvement in the dielectric properties of the dielectric layer, significant reductions in the
3 thickness, porosity, void space and interconnectedness of the void space of the layer, and an
4 improvement in the surface smoothness of the layer, leading to more uniform luminance and
5 reduced dielectric breakdown in electroluminescent displays formed therefrom.

6 Electroluminescent laminates made with the thick film dielectric as set forth in U.S.
7 Patent 5,432,015, generally show uniform luminosity as viewed by the naked eye, but when
8 viewed under a X100 microscope show a mottled appearance with some areas brightly
9 illuminated and other areas dimly illuminated or not illuminated at all. When the driving
10 voltage is near the threshold voltage this mottled appearance is most pronounced. The effect
11 is diminished as the voltage is increased above this value and all regions become illuminated.
12 The effect of this behavior is that the onset of luminosity occurs gradually as the voltage is
13 raised above the nominal threshold value and the rate of increase in the average luminosity
14 with increasing voltage is relatively low. The scale of the observed variability of the
15 luminosity is of the order of 10 μm . In contrast, electroluminescent laminates made with a
16 thick film dielectric layer which has been isostatically pressed prior to sintering, in
17 accordance with this invention, do not show this mottled characteristic of the luminosity near
18 the threshold voltage and increases nearly linearly up to about 50 volts above the threshold
19 voltage, so that the average luminosity at a fixed voltage above the threshold voltage is about
20 50% higher than for an otherwise identical electroluminescent laminate. "Uniform
21 luminosity", as used herein, means the luminosity resolved to a scale of about 10 μm appears
22 uniform.

23 Broadly stated, in one aspect of the invention there is provided a method of forming a
24 thick film dielectric layer in an EL laminate of the type including one or more phosphor layers
25 sandwiched between a front and a rear electrode, the phosphor layer being separated from the
26 rear electrode by the thick film dielectric layer, comprising:

27 depositing a ceramic material in one or more layers on a rigid substrate providing the
28 rear electrode, by a thick film technique, to form a dielectric layer having a thickness of 10 to
29 300 μm ;

30 pressing the dielectric layer to form a densified layer with reduced porosity and
31 surface roughness; and

32 sintering the dielectric layer to form a pressed, sintered dielectric layer which, in an

1 EL laminate, has an improved uniform luminosity over an unpressed, sintered dielectric layer
2 or the same composition.

3 In another broad aspect, the invention provides an improved combined substrate and
4 dielectric layer component for use in an EL laminate, comprising:

5 a rigid substrate providing a rear electrode;
6 a thick film dielectric layer on the substrate providing the rear electrode, the thick film
7 dielectric layer being formed from a pressed, sintered ceramic material having, compared to
8 an unpressed, sintered dielectric layer of the same composition, improved dielectric strength,
9 reduced porosity and uniform luminosity in an EL laminate.

10 In still a further broad aspect, the invention provides an EL laminate, comprising:

11 a planar phosphor layer;
12 a front and rear planar electrode on either side of the phosphor layer;
13 a rear substrate providing the rear electrode, the rear substrate having sufficient
14 mechanical strength and rigidity to support the laminate; and

15 a thick film dielectric layer on the substrate providing the rear electrode, the thick film
16 dielectric layer being formed from a pressed, sintered ceramic material having, compared to an
17 unpressed, sintered dielectric layer of the same composition, improved dielectric strength,
18 reduced porosity and uniform luminosity in an EL laminate.

19 The present invention further provides a patterned phosphor structure particularly
20 useful in AC thin film/thick film electroluminescent devices, and also useful in AC thin film
21 electroluminescent devices if the thickness of the phosphor over the sub-pixels is not too great.
22 In the phosphor structure of the invention, the emitted light from the phosphor underlying the
23 red, green and blue sub-pixels falls within a narrowed wavelength range of the visible
24 electromagnetic spectrum that more closely matches the range transmitted by the respective
25 filters. In this manner, both the luminosity and the energy efficiency of the display can be
26 substantially increased over the values achievable with a conventional colour by white
27 phosphor design. Another feature of the patterned phosphor structure of the present invention
28 is that the sub-pixel threshold voltages can be made equal and, the relative luminosities of the
29 sub-pixels can be set so that they bear set ratios to one another at each operating modulation
30 voltage used to generate the desired luminosities for red, green and blue. Preferably, the set
31 ratios remain substantially constant over the full range of the modulation voltage, for proper
32 colour balance. Most preferably, for a full colour display, the set luminosity ratios for the red,

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1 green and blue sub-pixels are in the ratio of about 3:6:1, or sufficiently close to this ratio so as
2 to enable adequate colour fidelity (gray scale).

3 To reduce the negative impact of the limitations inherent in filter characteristics, it is
4 desirable to use a phosphor for the blue sub-pixels that does not emit significant intensities of
5 green or red light. Cerium doped strontium sulfide (SrS:Ce), optionally codoped with
6 phosphorus, preferably prepared as set out herein, provides desirable CIE colour coordinates
7 and luminosity for the blue, and optionally for the green sub-pixels. For green sub-pixels,
8 manganese doped zinc sulfide (ZnS:Mn) does not generally provide an adequate luminosity
9 when filtered to provide acceptable colour coordinates, but in accordance with this invention,
10 it can be combined with cerium doped strontium sulfide to give higher luminosity with good
11 colour coordinates. Alternatively, $Zn_{1-x}Mg_xS:Mn$, which, with an appropriate ratio of Zn to
12 Mg, has a higher luminosity in the green region of the spectrum than does ZnS:Mn, can be
13 used for the green sub-pixels, optionally with ZnS:Mn. Either or both of the $Zn_{1-x}Mg_xS:Mn$ or
14 the ZnS:Mn phosphors can be used for the red sub-pixels, x being between 0.1 and 0.3.

15 In accordance with this invention, one or more means are included with the one or
16 more of the phosphor deposits for setting and equalizing the threshold voltages of the sub-
17 pixels, and for setting the relative luminosities of the sub-pixels so that they bear set ratios to
18 one another at each operating modulation voltage used to generate the desired luminosities for
19 red, green and blue. Threshold voltage means the highest amplitude of a voltage pulse that,
20 when applied to a sub-pixel at the desired repetition rate, generates a measurable filtered
21 luminosity less than the lowest specified gray scale luminosity for that sub-pixel. Thus, the
22 means for setting and equalizing the threshold voltages also functions to set the relative sub-
23 pixel luminosities so that they bear set ratios to one another over the full range of the
24 modulation voltage used. Generally, the means is one or more of (a) a threshold voltage
25 adjustment layer formed from a dielectric or semiconductor material which is located in one or
26 more of the positions of over, under and embedded within one or more of the phosphor
27 deposits, and/or (b) one or more of the phosphor deposits being formed with different
28 thicknesses.

29 It should be noted that the terms "sub-pixel" and "sub-pixel phosphor elements" are
30 used interchangeably herein to refer to the phosphor deposits for a particular red, green or blue
31 sub-pixel element, along with any threshold voltage adjustment deposit associated with that
32 sub-pixel element.

1 Appropriate colour filters can be chosen for the three sub-pixels to achieve self-
2 consistent optimization of luminosity and colour coordinates for each, and overall pixel energy
3 efficiency. The present invention has application to other colour phosphors, the strontium
4 sulfide and zinc sulfide phosphors being representative only. Usually, at least two different
5 phosphors are used, each being formed from different host materials. It is also possible to
6 extend the present invention to three or more different phosphor layers for further
7 optimization.

8 Broadly stated, the invention provides a patterned phosphor structure having red, green
9 and blue sub-pixel phosphor elements for an AC electroluminescent display, comprising:

10 at least a first and a second phosphor, each emitting light in different ranges of the
11 visible spectrum, but whose combined emission spectra contains red, green and blue light;

12 said at least first and second phosphors being in a layer, arranged in adjacent, repeating
13 relationship to each other to provide a plurality of repeating at least first and second phosphor
14 deposits; and

15 one or more means associated with one or more of the at least first and second
16 phosphor deposits, and which together with the at least first and second phosphor deposits,
17 form the red, green and blue sub-pixel phosphor elements, for setting and equalizing the
18 threshold voltages of the red, green and blue sub-pixel phosphor elements, and for setting the
19 relative luminosities of the red, green and blue sub-pixel phosphor elements so that they bear
20 set ratios to one another at each operating modulation voltage used to generate the desired
21 luminosities for red, green and blue.

22 Suitable materials for the threshold voltage adjustment layers are those which, when
23 deposited as a layer, at an appropriate thickness, will not conduct until the voltage across the
24 patterned phosphor structure exceeds the threshold voltage for an otherwise identical patterned
25 phosphor structure that does not include the threshold voltage adjustment layer. A suitable
26 material can be chosen by examination of its dielectric constant and dielectric breakdown
27 strength to meet the above condition, with materials having relatively high dielectric constants
28 and dielectric breakdown strengths as compared to those of the phosphor materials being
29 preferable. The materials for the threshold voltage adjustment layer are compatible with those
30 materials that are in contact with them in the patterned phosphor structure, and are chosen
31 from dielectric materials and semiconductors. By semiconductors is meant both intrinsic
32 semiconductors, and semiconductors with deep impurity levels that have effective electronic

1 band gaps that are comparable to, or larger than, the effective band gap of the phosphor
2 material. Examples of suitable materials include binary metal oxides such as alumina and
3 tantalum oxide, binary metal sulfides such as zinc sulfide and strontium sulfide, silica, and
4 silicon oxynitride. The suitability of these materials is dependent on the properties of the
5 interface between the materials and any phosphor materials and the dielectric materials in
6 contact with them. In general, when the phosphor deposit is of a phosphor which is based on
7 zinc sulfide, the preferred threshold voltage adjustment material is a binary metal oxide, most
8 preferably alumina.

9 Alternatively, or in addition, the means for setting and equalizing the threshold
10 voltages and for setting the relative luminosities comprises forming the first and second
11 phosphor deposits with different thicknesses so as to balance the threshold voltages and the
12 luminosities of the sub-pixel elements. In this case, the overall colour balance can be achieved
13 for a pixel by setting the luminosities for the sub-pixel by using different sub-pixel element
14 areas, for instance by making the sub-pixel elements of the less efficient phosphors wider than
15 the width of the sub-pixel elements with the more efficient phosphors.

16 The patterned phosphor structure of this invention allows for correct CIE colour
17 coordinates for a full colour display to be achieved for all operating modulation voltage
18 levels, while allowing for the equalizing of the threshold voltages of the sub-pixel elements.
19 The means for setting and equalizing the threshold voltages, and for setting the relative
20 luminosities of the red, green and blue sub-pixels may also comprise, in addition to the
21 threshold voltage adjustment deposits and/or altering the thicknesses of the phosphor deposits,
22 varying one or more of the following in order to set the relative luminosities:

- 23 i. the areas of the phosphor deposits; and
24 ii. the concentrations of a dopant or co-dopant in the phosphor deposits.

25 Preferably, the first and second phosphors are of different host materials, such as a
26 strontium sulfide phosphor or a zinc sulfide phosphor. Generally, a different host material
27 implies that a different element has been introduced to the phosphor host material at an atomic
28 percent greater than about 5 atomic percent. Preferred first and second phosphors are SrS:Ce
29 and ZnS:Mn; SrS:Ce and Zn_{1-x}Mg_xS:Mn; or SrS:Ce with layers of both ZnS:Mn and Zn_{1-x}Mg_xS:Mn, it being possible for the SrS:Ce to be codoped with phosphorus. These are
31 examples of zinc sulfide and strontium sulfide phosphors which, if they were superimposed,
32 would have a combined emission spectrum which covers the wavelengths of white light

1 (individual visible spectra for ZnS:Mn and SrS:Ce are shown in Figures 7 and 8 respectively).
2 Within the scope of the present invention, each of the first and second phosphor deposits may
3 comprise one or more layers of a same or different phosphor for each sub-pixel element, and
4 each of the phosphor deposits may themselves be composed of one or more phosphor
5 compositions (i.e. mixtures of more than one phosphors). As set out below, the phosphor
6 structure of this invention may be provided on one or more layers. For example, in a single
7 layer phosphor structure, as set forth in Example 3, the phosphors can be arranged such that
8 $Zn_{1-x}Mg_xS:Mn$ forms the red and green sub-pixel elements, while SrS:Ce forms the blue sub-
9 pixel element. A threshold voltage adjustment layer of a binary metal oxide such as alumina
10 can be provided over the red and green sub-pixel elements to achieve the desired luminous
11 intensity ratios between the sub-pixel elements. Alternatively, as set forth in Example 4,
12 SrS:Ce deposits can be used for the blue sub-pixel elements, and a layer of $Zn_{1-x}Mg_xS:Mn$
13 between layers of ZnS:Mn can be used for the red and green sub-pixel elements. The stacked
14 zinc sulfide phosphor deposits of this embodiment can be formed thick enough to equalize the
15 threshold voltages between the sub-pixel elements. To achieve the desired relative
16 luminosities between the sub-pixel elements, the SrS:Ce deposits for the blue sub-pixels can
17 be made wider than the sub-pixels for red and green. Alternatively, as set forth in Example 5,
18 SrS:Ce deposits can be used for both the green and blue sub-pixel elements, and ZnS:Mn can
19 be used for the red sub-pixel elements. A threshold voltage adjustment layer of a binary metal
20 oxide such as alumina can be used over the red sub-pixel deposits to equalize the threshold
21 voltages.

22 When two layers of phosphors are used, as in Example 2, the phosphors may be
23 arranged such that SrS:Ce is patterned in a first layer with ZnS:Mn or $Zn_{1-x}Mg_xS:Mn$, and a
24 second layer of SrS:Ce can be formed over the first layer. In this embodiment, the stacked
25 phosphor deposits of SrS:Ce form the blue sub-pixel elements, while the red and green sub-
26 pixel elements are formed by the stacked zinc sulfide phosphor deposit under the SrS:Ce
27 deposit.

28 Compared to conventional colour by white techniques in which the white light is
29 provided by coplanar, stacked layers of SrS:Ce and ZnS:Mn, the patterned phosphor structure
30 of the present invention has the advantage of being able to provide a thicker layer of SrS:Ce
31 for the blue sub-pixel element, without having an over- or under- layer of ZnS:Mn. This
32 results in increased blue luminance and, since there is no yellow-orange light being emitted in

1 the blue sub-pixels, the filtered light from the SrS:Ce phosphor is a more saturated blue.

2 The patterned phosphor structure of this invention has particular application in hybrid
3 thick film/thin film AC electroluminescent devices such as described in U.S. Patent 5,432,015,
4 in which the EL laminate is fabricated on a rigid rear substrate, with a thick film dielectric
5 layer below the phosphor structure. AC thin film electroluminescent devices (TFELs) have
6 the disadvantage of generally requiring its thin layers to be planarized, that is of even
7 thicknesses. Such devices generally preclude the ability to use colour phosphor sub-pixels of
8 differing thicknesses. However, using a thick film dielectric layer in an EL laminate in
9 combination with the patterned phosphor structure of the present invention allows one to use
10 different thicknesses of the individual phosphor sub-pixel deposits, so as to optimize the
11 colour coordinates and luminosity of a particular sub-pixel element, while still setting and
12 equalizing the threshold voltages for the sub-pixel elements.

13 The present invention also extends to novel methods for fabricating the patterned
14 phosphor structure of the present invention. Broadly stated, the invention provides a method
15 of forming a patterned phosphor structure having red, green and blue sub-pixel elements for an
16 AC electroluminescent display, comprising:

17 selecting at least a first and a second phosphor, each emitting light in different ranges
18 of the visible spectrum, but whose combined emission spectra contains red, green and blue
19 light;

20 depositing and patterning said at least first and second phosphors in a layer to form a
21 plurality of repeating at least first and second phosphor deposits arranged in adjacent,
22 repeating relationship to each other; and

23 providing one or more means associated with one or more of the at least first and
24 second phosphor deposits, and which together with the at least first and second phosphor
25 deposits, form the red, green and blue sub-pixel phosphor elements, for setting and equalizing
26 the threshold voltages of the red, green and blue sub-pixel phosphor elements, and for setting
27 the luminosities of the red, green and blue sub-pixel elements so that they bear set relative
28 luminosities to one another at each operating modulation voltage used to generate the desired
29 luminosities for red, green and blue; and

30 optionally annealing the patterned phosphor structure so formed.

31 Preferably the patterning of the at least first and second phosphor is achieved by
32 photolithographic techniques, including the steps of:

- 1 a) depositing a layer of the first phosphor which is to form at least one of the red, green
2 and blue sub-pixel elements;
3 b) removing the first phosphor material in regions which are to define the other of the
4 red, green and blue sub-pixel elements, leaving spaced first phosphor deposits;
5 c) depositing the second phosphor over the first phosphor deposits and in the regions
6 which are to define the other of the red, green and blue sub-pixel elements; and
7 d) removing the second phosphor from above the first phosphor deposits, leaving a
8 plurality of repeating first and second phosphor deposits arranged in adjacent, repeating
9 relationship to each other.

10 Novel photolithographic techniques have been developed which are particularly useful
11 in patterning strontium and zinc sulfide phosphors, but which have application to other
12 phosphor combinations. In its most preferred embodiments, the photolithographic methods of
13 this invention utilizes a negative photoresist, and has the advantage of needing only one photo-
14 mask to accomplish the patterning of the red, green and blue sub-pixel elements. In
15 accordance with this method, steps b) through d) include, applying a negative resist to the
16 first phosphor; exposing and developing the resist through a photo-mask in the areas that the
17 first phosphor is to define one or more of the red, green and blue sub-pixel elements; removing
18 the first phosphor as in step b), depositing the second phosphor over the first phosphor
19 deposits and in the regions which are to define the other of the red, green and blue sub-pixel
20 elements; and then removing, by lift-off, the second phosphor from above the first phosphor
21 deposits. Typically in this method, the first phosphor is a strontium sulfide phosphor, most
22 preferably SrS:Ce, which forms the blue sub-pixel elements and optionally the green sub-pixel
23 elements, and the second phosphor is a zinc sulfide phosphor, most preferably ZnS:Mn or Zn_{1-x}Mg_xS:Mn, or both, which forms the red, and optionally the green, sub-pixel elements. In
25 accordance with the method, the means for setting and equalizing the threshold voltages and
26 for setting the luminosities of the sub-pixel elements can include adding a threshold voltage
27 adjustment deposit beneath, within or above one or more of the phosphor deposits and/or
28 forming the phosphor deposits with different thicknesses, as set out above. In addition, the
29 means for setting and equalizing the threshold voltages, and for setting the luminosities, of the
30 sub-pixel elements may include varying one or more of:
31 i. the areas of the phosphor deposits; and
32 ii. the concentrations of a dopant or co-dopant in the phosphor deposits.

1 The invention also provides a novel photolithographic technique which is particularly
2 useful for patterning a phosphor which is subject to hydrolysis, such as alkaline earth metal
3 sulfide or selenide phosphors. Broadly, the invention provides a method of forming a
4 patterned phosphor structure having red, green and blue sub-pixel elements for an AC
5 electroluminescent display, comprising:

6 a) selecting at least a first and a second phosphor, each emitting light in different
7 ranges of the visible spectrum, but whose combined emission spectra contains red, green and
8 blue light;

9 b) depositing a layer of the first phosphor which is to form at least one of the red, green
10 or blue sub-pixel elements;

11 c) applying a photo-resist to the first phosphor, exposing the photo-resist through a
12 photo-mask, developing the photo-resist, and removing the first phosphor in regions that the
13 first phosphor is to define as one or more of the red, green and blue sub-pixel elements,
14 leaving spaced first phosphor deposits, wherein the first phosphor is removed with an etchant
15 solution comprising a mineral acid, or a source of anions of a mineral acid, in a non-aqueous,
16 polar, organic solvent which solubilizes the reaction product of the first phosphor with anions
17 of the mineral acid, and wherein optionally, prior to removing the first phosphor with the
18 etchant solution, the first phosphor layer is immersed in the non-aqueous organic solvent;

19 d) depositing the second phosphor material over the first phosphor deposits and in
20 regions which are to define the other of the red, green and blue sub-pixel elements; and

21 e) removing by lift-off, the second phosphor material and the resist from above the first
22 phosphor deposits leaving a plurality of repeating first and second phosphor deposits arranged
23 in adjacent, repeating relationship to each other.

24 The invention also extends to EL laminates combining, as described above, a rigid rear
25 substrate, a thick film dielectric layer and the patterned phosphor structure, together with front
26 and rear column and row electrodes on either side of the phosphor layer, in which the front and
27 rear column and row electrodes are generally aligned with the phosphor sub-pixel elements,
28 and bandpass colour filter means aligned with the red, green and blue phosphor sub-pixel
29 elements for passing therethrough red, green and blue light emitted from the phosphor sub-
30 pixel elements.

31 Another aspect of the present invention provides novel and separate selection criteria
32 for barrier diffusion layers and injection layers useful with electroluminescent phosphors, and

1 particularly useful with the patterned phosphor structure and the thick film dielectric of the
2 present invention. Preferably, a diffusion barrier layer is included above the thick film
3 dielectric layer, or if present, above the second ceramic material. The diffusion barrier layer is
4 composed of a metal-containing electrically insulating binary compound which is compatible
5 with any adjacent layers, and which is precisely stoichiometric, preferably varying from its
6 precise stoichiometric composition by less than 0.1 atomic percent, and having a thickness of
7 100 to 1000 Å. Preferred materials will vary with the particular phosphors and the materials in
8 the dielectric layers, but most preferred materials are alumina, silica and zinc sulfide.
9 Preferably, an injection layer is included above the thick film dielectric layer, or if present,
10 above the second ceramic material or the barrier diffusion layer, to provide a phosphor
11 interface. The injection layer is composed of a binary dielectric or semi-conductor material
12 which is non-stoichiometric in its composition and which has electrons in a preferred range of
13 energy for injection into the phosphor layer. The material is compatible with adjacent layers
14 and is preferably non-stoichiometric by greater than 0.5 atomic percent. Preferred materials
15 vary with the particular phosphor and the materials in the underlying dielectric layers, but
16 preferred materials for providing optimum electron energies are hafnia or yttria. There is a
17 compromise between optimum electron injection and compatibility with adjacent layers. As a
18 result, sometimes a non-stoichiometric compound cannot be used as an injection layer.

19 Another broad aspect of the invention provides a method of synthesizing strontium
20 sulfide, comprising:

21 providing a source of high purity strontium carbonate in a dispersed form;
22 heating the strontium carbonate in a reactor with gradual heating up to a maximum
23 temperature in the range of 800 to 1200°C;
24 contacting the heated strontium carbonate with a flow of sulfur vapours formed heating
25 elemental sulfur in the reactor to at least 300°C in an inert atmosphere; and
26 terminating the reaction by stopping the flow of sulfur at a point when sulfur dioxide or
27 carbon dioxide in the reaction gas reaches an amount which correlates with an amount of
28 oxygen in oxygen-containing strontium compounds in the reaction product which is in the
29 range of 1 to 10 atomic percent.

30 By "dispersed form", in reference to the source of strontium carbonate, as used herein
31 and in the claims, is meant that the strontium carbonate powder particles are exposed to the
32 process conditions substantially uniformly. This can preferably be achieved by using small

1 batches, using volatile, non-contaminating, clean evaporating compounds or solvents which
2 decompose into gaseous products prior to the onset of the reaction, using fluidized beds or
3 tumbler reactors.

4 The term "phosphor" as used herein and in the claims, means a substance which
5 provides electroluminescence when a sufficient electric field is applied across it, and electrons
6 are injected into it.

7 The term "white light" when used herein and in the claims, when referring to the
8 combined emission spectra of two or more phosphors, means that white light is emitted when
9 the phosphors are superimposed in a manner such that the light can be filtered to provide red,
10 green and blue light.

11 The term "compatible" when used herein and in the claims, means that the material is
12 chemically stable to that it does not chemically react with adjacent layers.

13 BRIEF DESCRIPTION OF THE DRAWINGS

14 Figure 1 is a schematic sectional view of an EL laminate having a thick film dielectric
15 of the present invention with conventional colour by white bilayer phosphors and red, green
16 and blue filters;

17 Figure 2 is a schematic sectional view of an EL laminate having a thick film dielectric
18 of the present invention combined with a two layer patterned phosphor structure of the present
19 invention;

20 Figure 3 is a graph comparing the unfiltered luminance plotted against voltage for the
21 colour by white structure of Figure 1 (shown in dotted line in the graph) and the patterned
22 phosphor structure of Figure 2 (shown in solid lines in the graph), at a driving frequency of 60
23 Hz;

24 Figure 4 is a graph comparing the filtered luminances plotted against voltage for the
25 colour by white structure of Figure 1 and the patterned phosphor structure of Figure 2, at a
26 driving frequency of 60 Hz:

27 Figure 5 is a plan view of the ITO column electrode over several pixels, showing
28 alignment with the underlying red, green and blue phosphor sub-pixel elements;

29 Figure 6 is a schematic sectional view of a single pixel of an EL laminate with a two
30 layer patterned phosphor structure of the present invention with additional diffusion barrier
31 and injection layers;

32 Figure 7 is a graph of the emission spectrum for ZnS:Mn, plotting intensity in arbitrary

1 units against wavelength in nanometres;

2 Figure 8 is a graph of the emission spectrum for SrS:Ce, when synthesized by the
3 process of the present invention, plotting intensity in arbitrary units against wavelength in
4 nanometres; and

5 Figure 9 is a schematic plot of energy against distance to illustrate phosphor electron
6 bands in the presence of an electric field.

7 The figures showing the thick film dielectric layers and the patterned phosphor
8 structures of this invention are not shown to scale.

9 DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 EL Laminate With Isostatic Pressed Thick Film Dielectric

11 The present invention provides a thick film dielectric layer having increased dielectric
12 strength and dielectric constant, significantly reduced void space, void interconnectedness,
13 porosity and thickness, and significantly improved surface smoothness, when compared to the
14 thick films dielectric layers such as described in U.S. Patent 5,432,015. The smoother surface
15 of the dielectric layer results in an unexpected improvement by providing a higher and more
16 uniform luminosity across an EL display formed therefrom. The improvement is achieved by
17 compressing a thick film dielectric layer prior to sintering, such as by isostatic pressing.

18 The thick film dielectric layer will be described with reference to Figures 1, 2, 5 and 6.
19 An EL laminate 10 is built from the rear to the front (viewing) side on a rear substrate 12.
20 Preferably, the substrate 12 is a rigid substrate such as a preformed sheet, providing sufficient
21 mechanical strength and rigidity to support the laminate 10. Alternatively, the substrate 12
22 could be a green tape or the like which will sinter to provide the rigidity for the laminate 10.
23 Thus, the term "rigid substrate" as used herein refers to the substrate after sintering. The
24 substrate 12 is preferably formed from a ceramic which can withstand the high sintering
25 temperatures (typically up to 1000°C) used in processing other layers of the laminate 10. An
26 alumina sheet is most preferred, having a thickness and rigidity sufficient to support the EL
27 laminate 10. A rear electrode layer 14 is formed on the substrate 12. For lamp applications,
28 the rear substrate 12 and rear electrode 14 might be integral, for example by being provided by
29 a rigid, electrically conductive metal sheet. For display applications, the rear electrode 14
30 consists of rows of conductive metal address lines centered on the substrate 12 and spaced
31 from the substrate edges. Preferably conductive metal address lines are screen printed from
32 noble metal pastes, as is well known. An electrical contact tab 16 protrudes from the electrode

1 14, as seen in Figure 5. The thick film dielectric layer 18 is formed above the electrode 14,
2 and may be formed as a single layer, or as multiple layers. In Figures 1 and 2, the layer is
3 shown schematically as one layer, while in Figure 6, the layer comprises a thicker, first
4 dielectric layer 18, and a thinner, second dielectric layer 20. One or more phosphor layers 22
5 are provided above the dielectric layer 18, or dielectric layers 18, 20. In Figure 1, the
6 phosphor is shown as two layers as in a conventional colour by white design. In Figure 2 and
7 6, the phosphor layer 22 is shown to comprise a patterned phosphor structure 30 of the present
8 invention, as is described in greater detail below. Above the phosphor layer(s) 22, there may
9 be provided a third dielectric layer 23. Above the optional third dielectric layer 23 is a front,
10 transparent electrode layer 24. The front electrode layer 24 is shown in Figures 1 and 2 as
11 solid, but in actuality, for display applications, it consists of columns of address lines arranged
12 perpendicularly to the row address lines of the rear electrode 14. The front electrode 24 is
13 preferably formed from indium tin oxide (ITO) by known thin film or photolithographic
14 techniques. Although not shown, the front electrode is also provided with an electrical contact.
15 Figures 1 and 2 show bandpass colour filter means 25 above the ITO lines, such as polymeric
16 red, green and blue filters 25a, 25b, and 25c respectively, aligned with the ITO address lines.
17 In Figure 2, these filters 25a, 25b, and 25c are also aligned with red, green and blue phosphor
18 sub-pixel elements 30a, 30b and 30c, in the patterned phosphor structure 30. Also not shown,
19 the EL laminate 10 is encapsulated with a transparent sealing layer to prevent moisture
20 penetration. The EL laminate 10 is operated by connecting an AC power source to the
21 electrode contacts. Voltage driving circuitry (not shown) is well known in the art. The EL
22 laminate 10, incorporating the thick film dielectric layer 18, has application in both EL lamps
23 and displays.

24 It will be understood by persons skilled in the art that further intervening layers,
25 including for example one or more barrier diffusion layers 26, injection layers 28 or dielectric
26 layers (such as optional second and third dielectric layers 20, 23, respectively) can be included
27 in the laminate 10, some of which are described more particularly below in association with
28 the patterned phosphor structure 30. Thus, throughout this description and in the patent
29 claims, when an EL laminate is defined as including certain layers, additional, intervening
30 layers are not meant to be excluded.

31 It will be appreciated that, in general, the criteria for establishing the thickness and
32 dielectric constant of the dielectric layer(s) are calculated so as to provide adequate dielectric

1 strength at minimal operating voltages. The criteria are interrelated as set forth below, in
2 respect of a single phosphor layer and a single dielectric layer. In the case of multilayers, such
3 as a two layer phosphor, or the patterned phosphor structure described below, the criteria are
4 adjusted for the multiple layers, for example by using the thickest dimension and average
5 dielectric constant of the entire phosphor layer.

6 Given a typical range of thickness for the phosphor layer (d_1) of between about 0.2 and
7 2.5 microns, a dielectric constant range for the phosphor layer (k_1) of between about 5 and 10
8 and a dielectric strength range for the dielectric layer(s) of about 10^6 to 10^7 V/m, the following
9 relationships and calculations can be used to determine typical thickness (d_2) and dielectric
10 constant (k_2) values for the dielectric layer of the present invention. These relationships and
11 calculations may be used as guidelines to determine d_2 and k_2 values, without departing from
12 the intended scope of the present invention, should the typical ranges change significantly.

13 The applied voltage V across a bilayer comprising a uniform dielectric layer and a
14 uniform non-conducting phosphor layer sandwiched between two conductive electrodes is
15 given by equation 1:

16
$$V = E_2 * d_2 + E_1 * d_1 \quad (1)$$

17 wherein:

18 E_2 is the electric field strength in the dielectric layer;

19 E_1 is the electric field strength in the phosphor layer;

20 d_2 is the thickness of the dielectric layer; and

21 d_1 is the thickness of the phosphor.

22 In these calculations, the electric field direction is perpendicular to the interface
23 between the phosphor layer and the dielectric layer. Equation 1 holds true for applied voltages
24 below the threshold voltage at which the electric field strength in the phosphor layer is
25 sufficiently high that the phosphor begins to break down electrically and the device begins to
26 emit light.

27 From electromagnetic theory, the component of electric displacement D perpendicular
28 to an interface between two insulating materials with different dielectric constants is
29 continuous across the interface. This electric displacement component in a material is defined
30 as the product of the dielectric constant and the electric field component in the same direction.
31 From this relationship equation 2 is derived for the interface in the bilayer structure:

32
$$k_2 * E_2 = k_1 * E_1 \quad (2)$$

1 wherein:

2 k_2 is the dielectric constant of the dielectric material; and

3 k_1 is the dielectric constant of the phosphor material.

4 Equations 1 and 2 can be combined to give equation 3:

5
$$V = (k_1 * d_2 / k_2 + d_1) * E_1 \quad (3)$$

6 To minimize the threshold voltage, the first term in equation 3 needs to be as small as
7 is practical. The second term is fixed by the requirement to choose the phosphor thickness to
8 maximize the phosphor light output. For this evaluation the first term is taken to be one tenth
9 the magnitude of the second term. Substituting this condition into equation 3 yields equation
10 4:

11
$$d_2 / k_2 = 0.1 * d_1 / k_1 \quad (4)$$

12 Equation 4 establishes the ratio of the thickness of the dielectric layer to its dielectric
13 constant in terms of the phosphor properties. This thickness is determined independently from
14 the requirement that the dielectric strength of the layer be sufficient to hold the entire applied
15 voltage when the phosphor layer becomes conductive above the threshold voltage. The
16 thickness is calculated using equation 5:

17
$$d_2 = V / S \quad (5)$$

18 wherein:

19 S is the strength of the dielectric material.

20 Use of the above equations and reasonable values for d_1 , k_1 , and S provides the range
21 of dielectric layer thickness and dielectric constant. In general, the lower limit of the thickness
22 of the dielectric layer is that it must be sufficiently thick that the dielectric strength of the
23 dielectric layer is higher than the actual electric field present during operation of the device.
24 Generally, the combined thickness of the dielectric layers 18 and 20 can be as low as about 10
25 μm , with a phosphor layer thicknesses as high as about 2.5 μm .

26 A method of constructing the thick film dielectric layer 18 will now be described with
27 preferred materials and process steps.

28 The dielectric layer 18 is deposited by thick film techniques which are well known in
29 the electronics/semiconductor industries. The layer 18 is preferably formed from a
30 ferroelectric material, most preferably one having a perovskite crystal structure, to provide a
31 high dielectric constant compared to that of the phosphor layer(s) 22. The material will have a
32 minimum dielectric constant of 500 over a reasonable operating temperature for the laminate

10 (generally 20 - 100°C). More preferably, the dielectric constant of the dielectric layer
material is 1000 or greater. Exemplary materials for the layer include BaTiO₃, PbTiO₃, lead
magnesium niobate (PMN) and PMN-PT, a material including lead and magnesium niobates
and titanates, the latter being most preferred. Such materials may be formulated from their
dielectric powders, or may be obtained as commercial pastes.

Thick film deposition techniques are known in art, such as green tapes, roll coating,
and doctor blade application, but screen printing is most preferred. Commercially available
dielectric pastes can be used, with the recommended sintering steps set out by the paste
manufacturers. Pastes should be chosen or formulated to permit sintering at a high
temperature, typically about 800 - 1000°C. The dielectric layer 18 is screen printed in single
or multiple layers. Multiple layers are preferred, following each deposition with drying or
baking or sintering in order to achieve low porosity, high crystallinity and minimal cracking.
The deposited thickness of the dielectric layer 18 (i.e. prior to pressing) will vary with its
dielectric constant after sintering, and with the dielectric constant and thickness of the
phosphor layer(s) 22, and of the second dielectric layer 20. The deposited thickness will also
vary according to the degree of increased dielectric strength that is accomplished by the
subsequent isostatic pressing and sintering steps. Generally the deposited thickness of the
dielectric layer 18 will be in the range of 10 to 300 µm, more preferably 20 - 50 µm, and most
preferably 25 - 40 µm.

Pressing is preferably accomplished by cold isostatic pressing the combined substrate,
electrode, dielectric layer part at a high pressure such as 10,000 - 50,000 psi (70,000 - 350,000
kPa), prior to sintering the material, while encapsulating the part in a sealed bag with non-stick
materials in contact with the dielectric layer 18.. The thickness is preferably reduced by 20 to
50%, preferably about 30 - 40%, with a preferred thickness being about 10 - 20 µm (all
numbers referred to are after sintering). This is found to reduce the surface roughness by
about a factor of 10 and the surface porosity by about 50%, after sintering. The final porosity
is less than 20% after sintering. The dielectric strength has been shown to be improved by a
factor of 1.5 or more after sintering. Dielectric strengths greater than 5.0 x 10⁶ are achieved
after sintering. EL displays formed from isostatically pressed thick film dielectric layers in
accordance with the present invention have demonstrated higher luminosity and more uniform
luminosity across the display, and the thick film dielectric layers, once pressed, have a much
reduced sensitivity to dielectric breakdown due to printing defects.

1 A thinner, second dielectric layer 20 is preferably provided above the pressed and
2 sintered dielectric layer 18 to provide a smoother surface. It is formed from a second ceramic
3 material which may have a dielectric constant less than that of the dielectric layer 18. A
4 thickness of about 1 - 10 μm , and preferably about 1 - 3 μm is usually sufficient. The desired
5 thickness of this second dielectric layer 20 is generally a function of smoothness, that is the
6 layer may be as thin as possible, provided a smooth surface is achieved. To provide a smooth
7 surface, sol gel deposition techniques are preferably used, also referred to a metal organic
8 deposition (MOD), followed by high temperature heating or firing, in order to convert to a
9 ceramic material. Sol gel deposition techniques are well understood in the art, see for example
10 "Fundamental Principles of Sol Gel Technology", R.W. Jones, The Institute of Metals, 1989.
11 In general, the sol gel process enables materials to be mixed on a molecular level in the sol
12 before being brought out of solution either as a colloidal gel or a polymerizing
13 macromolecular network, while still retaining the solvent. The solvent, when removed, leaves
14 a solid ceramic with a high level of fine porosity, therefore raising the value of the surface free
15 energy, enabling the solid to be fired and densified at lower temperatures than obtainable using
16 most other techniques.

17 The sol gel materials are deposited on the first dielectric layer 18 in a manner to
18 achieve a smooth surface. In addition to providing a smooth surface, the sol gel process
19 facilitates filling of pores in the sintered thick film layer. Spin deposition or dipping are most
20 preferred. For spin deposition, the sol material is dropped onto the first dielectric layer 18
21 which is spinning at a high speed, typically a few thousand RPM. The sol can be deposited in
22 several stages if desired. The thickness of the layer 20 is controlled by varying the viscosity of
23 the sol gel and by altering the spinning speed. After spinning, a thin layer of wet sol is formed
24 on the surface. The sol gel layer 20 is heated, generally at less than 1000°C, to form a ceramic
25 surface. The sol may also be deposited by dipping. The surface to be coated is dipped into the
26 sol and then pulled out at a constant speed, usually very slowly. The thickness of the layer is
27 controlled by altering the viscosity of the sol and the pulling speed. The sol may also be
28 screen printed or spray coated, although it may be more difficult to control the thickness of the
29 layer with these techniques.

30 The ceramic material used in the second dielectric layer 20 is preferably a ferroelectric
31 ceramic material, preferably having a perovskite crystal structure to provide a high dielectric
32 constant. The dielectric constant is preferably similar to that of the first dielectric layer

1 material in order to avoid voltage fluctuations across the two dielectric layers 18, 20.
2 However, with a thinner layer being utilized in the second dielectric layer 20, a dielectric
3 constant as low as about 20 may be used, but will preferably be greater than 100. Exemplary
4 materials include lead zirconate titanate (PZT), lead lanthanum zirconate titanate (PLZT), and
5 the titanates of Sr, Pb and Ba used in the first dielectric layer 18, PZT and PLZT being most
6 preferred.

7 The next layer to be deposited may be one or more phosphor layers 22, as set out
8 above, and hereinbelow. However, it is possible, within the scope of this invention to include
9 additional layers of for diffusion barrier and injectivity purposes, as set out below. Phosphor
10 layers 22 may be deposited by known thin film deposition techniques such as vacuum
11 evaporation with an electron beam evaporator, sputtering etc. Particularly preferred is the
12 patterned phosphor structure of the present invention, as described hereinbelow.

13 A further transparent dielectric layer 23 above the phosphor layers 22 may be included,
14 if desired, followed by the front electrode 24. The EL laminate 10 may be annealed and then
15 sealed with a sealing layer (not shown) such as glass.

16 Diffusion Barrier Layer

17 The invention preferably provides a diffusion barrier layer 26 above the thick film
18 dielectric layer(s) 18, 20 and below the phosphor layer(s) 22, particularly the patterned
19 phosphor structure 30 described below. The diffusion barrier layer is preferably provided on
20 both sides of the phosphor layer(s) 22, as shown in Figure 6. Alternatively, the diffusion
21 barrier layer can be provided within the patterned phosphor structure of this invention, as set
22 out in the examples below.

23 A good diffusion barrier should be free of cracks and pinholes. These can be
24 eliminated through thermal expansion coefficient matching, stress relief, and conformal
25 coating techniques. There still may be residual diffusion due to grain boundary diffusion
26 which is dependent on the size and nature of the grains comprising the film, or crystal lattice
27 diffusion, which depends on the density of atomic vacancies. Diffusion through pinholes and
28 cracks can be distinguished from grain boundary or lattice diffusion in that it should result in
29 spatial variation of luminosity on the scale of the pinholes or cracks which increases with time
30 rather than spatially uniform time degradation in luminosity. Grain boundary diffusion, which
31 is generally much faster than crystal lattice diffusion, can be minimized by ensuring that the
32 deposited grains in the diffusion barrier layer are as large as possible. This minimizes the areal

1 density of grain boundaries. Chemical inertness of the barrier films in contact with the
2 immediately adjacent layers is also desired to preserve the integrity of the barrier layer.

3 Phosphor luminosity stability is improved when silica, alumina or zinc sulfide
4 diffusion barrier layers are used, rather than hafnia or yttria. The improvement results even if
5 a thin 100 Å injection layer 28, comprising a different material, is interposed between the
6 barrier layer 26 and the phosphor structure 30. Thus, in accordance with the present invention,
7 the diffusion barrier layer 26 is formed from compounds which have precise stoichiometric
8 compositions. The phase diagrams for the silicon-oxygen, aluminum-oxygen and zinc-sulphur
9 binary systems show that alumina, silica, and zinc sulfide exist only as precisely stoichiometric
10 compounds. By contrast, the yttria-oxygen and hafnium-oxygen phase diagrams show that
11 yttria can exist up to about 1 atomic percent deficient in oxygen, and hafnia can exist up to
12 about 3 atomic percent deficient in oxygen. Thus, these latter two materials, when deposited
13 as coatings, likely have a significant oxygen deficiency. Comparison of the experimental
14 stability data with the stoichiometry of the diffusion barrier layer provides evidence that
15 precise stoichiometric ceramic materials provide effective diffusion barriers.

16 Based on the above, materials suitable as diffusion barriers can be predicted. Metal-
17 containing electrically insulating binary compounds (dielectrics) that are inert in the presence
18 of adjacent layers and can be deposited without cracks or pinholes and are precisely
19 stoichiometric are preferred materials. The latter aspect can be ascertained by examining
20 binary phase diagrams for materials. Compounds providing the lowest lattice diffusion are
21 those for which the compounds exist only over a very small range of the ratio of their
22 constituent elements, preferably less than 0.1 atomic percent deviation from the stoichiometric
23 ratio. A deviation from the stoichiometric ratio will entail the formation of vacancies in place
24 of the deficient element. Among the materials known in the art as dielectric materials for
25 electroluminescent displays, alumina, silica and zinc sulfide are examples of such
26 stoichiometric compounds.

27 **Injection Layer**

28 The present invention may include an injection layer 28 above the diffusion barrier
29 layer 26, next to the phosphor layer(s) 22, particularly with the patterned phosphor structure 30
30 described below. The layer is preferably provided on both sides of the phosphor layer(s) 22, in
31 contact with the phosphor layer(s) 22. Alternatively, or as well, the injection layer may be
32 provided within the patterned phosphor structure of this invention, as set out in the examples

1 below.

2 A feature of this invention is the discovery that the selection criteria for injection layer
3 materials are different than for diffusion barrier materials, so a better combined utility can be
4 obtained by providing the diffusion barrier and injection layer characteristics using two distinct
5 layers for these functions. This does not preclude the possibility that with some thick film
6 dielectric compositions and/or some phosphor compositions, acceptable diffusion barrier and
7 injection characteristics might be found in the same material.

8 The purpose of this layer is to provide efficient injection characteristics for electrons
9 injected into the phosphor. The purpose is to maximize the number of electrons per unit area
10 of the phosphor that are injected into the phosphor within a preferred energy range so as to
11 maximize the electro-optical energy efficiency associated with the injection of electrons into
12 the phosphor and the subsequent conversion of that energy into light. Generally, this can be
13 accomplished by designing the injection layer phosphor interface so that a maximum number
14 of electrons at the interface are in states with a narrow range of energies that result in the most
15 efficient electro-optic efficiency. The literature reveals data on a large number of such
16 interfaces. With ZnS phosphors, it is found that hafnia and yttria provide higher injection
17 efficiencies than do silica and alumina. With SrS:Ce, it is found that pure ZnS provides a
18 somewhat higher efficiency than does alumina, hafnia, or silica, although this may be because
19 ZnS has a better compatibility with SrS:Ce, making the ZnS layer more of a diffusion barrier
20 layer in its function. In general, the injection layer 28 is a dielectric, binary material which is
21 non-stoichiometric in its composition, that is having greater than about 0.5% atomic deviation
22 from its stoichiometric ratio, so as to have more electrons within a preferred range of energy
23 for better injection efficiency.

24 **Patterned Phosphor Structure**

25 The patterned phosphor structure of this invention is shown generally at 30 in Figures
26 2, 5 and 6. It is described below in the examples, Example 2 being directed to a two layer
27 patterned phosphor structure, and Examples 3, 4 and 5 being directed to a single layer
28 patterned phosphor structure.

29 An EL laminate 10 incorporating the patterned phosphor structure 30 of the present
30 invention will preferably include all of the layers of the EL laminate 10 as set out above. The
31 description of the patterned phosphor structure 30 is provided for one or a few pixels, but of
32 course multiple pixels are repeated cyclically across the EL laminate 10 of an EL display. In

1 that respect, three sub-pixels of row and column electrodes together form a single pixel,
2 aligned with the red, blue and green phosphor sub-pixel elements 30a, 30b and 30c
3 respectively, and the red, blue and green filters 25a, 25b, and 25c respectively.

4 The patterned phosphor structure 30 is formed on the dielectric layer 18 or 20, or more
5 preferably above any barrier diffusion and injection layers 26 and 28, by depositing and
6 patterning two or more phosphors emitting light in different ranges of the visible spectrum in
7 at least one layer to form a plurality of repeating phosphor deposits arranged in adjacent,
8 repeating relationship to each other. The patterning may be accomplished by photolithography
9 or by shadow mask patterning, however photolithography is preferred. In accordance with this
10 invention, a photolithography method with a negative photoresist and lift-off procedure
11 involving as few as one photo-mask is used. This process is particularly advantageous for
12 patterning moisture sensitive strontium sulfide phosphors along with zinc sulfide phosphors,
13 but has application for other colour phosphors, particularly for alkaline earth metal sulfide or
14 selenide phosphors which are subject to hydrolysis.

15 A first layer of a first phosphor is deposited by known techniques to form one or more
16 of the red, green or blue sub-pixel elements. Preferably, the first layer is a strontium sulfide
17 phosphor, to form the blue, or the blue and the green sub-pixel elements. A negative
18 photoresist is applied to this first phosphor layer, followed by exposure through a photo-mask
19 designed to expose either the blue, or the blue and green, sub-pixel elements.

20 A negative resist is used due to its superior stability at the elevated temperatures to
21 which the resist is exposed during subsequent processing, and its ability to be used with non-
22 aqueous solutions. A negative resist based on polyisoprene is preferred. Alternative negative
23 resists such as those based on polyimide can also be used, as can positive resists if they are
24 first subject to deep ultraviolet curing before being exposed to high temperature. Positive
25 resists that can be exposed using e-beam writing rather than light exposure may also be used,
26 particularly if very high resolution patterning is desired.

27 The exposure process requires the use of only one mask through all of the phosphor
28 patterning steps, simplifying the process over multi-mask processes commonly used in
29 photolithography. Negative resists have the property that they can be rendered insoluble in
30 developer chemicals when they are exposed to light. Accordingly, the patterning mask is
31 designed to allow exposure of the resist over the regions corresponding to the blue, or the blue
32 and green, sub-pixel elements.

1 Following exposure, the resist is developed, rinsed and de-scummed, prior to acid
2 etching to remove the phosphor in the regions which are to form the red and green, or the red,
3 sub-pixel elements. Etching is preferably preceded by first immersing in a polar, non-aqueous,
4 organic solvent, preferably methanol, in order to permeate the pores of the phosphor. Etching
5 is accomplished with an etchant solution which includes a mineral acid, or a source of anions
6 of a mineral acid, in a non-aqueous, polar, organic solvent which solubilizes the reaction
7 product of the first phosphor with anions of the mineral acid. By non-aqueous is meant a
8 solvent which has less than 1% by volume water, preferably less than 0.5% water. Mineral
9 acids include hydrofluoric acid, hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid,
10 and hydrobromic acid, or mixtures thereof, with hydrochloric acid and phosphoric acid being
11 most preferred. The non-aqueous, polar, organic solvent is most preferably methanol. The
12 mineral acid is preferably used from its concentrated form in the etchant solution in order to
13 limit the amount of water which is included. Generally, the amount of concentrated mineral
14 acid is in the range of 0.1 to 1% by volume. The part with the first phosphor is immersed in
15 this etchant solution to dissolve the areas of unexposed strontium sulfide. Etchant solutions of
16 0.5% HCl in methanol, or 0.1% HCl and 0.1% H_3PO_4 in methanol, are exemplary of preferred
17 embodiments.

18 A second phosphor, or optionally a second and a third phosphor, for the red and green,
19 or the red, sub-pixel elements is deposited over both the first phosphor, overlaid with the
20 exposed resist, and the regions where the first phosphor has been removed. Preferably the
21 second, or second and third, phosphors are zinc sulfide phosphors. At this point, additional
22 layers such as injection layers, or threshold voltage adjustment layers may be deposited above
23 the second, or above the second and third, phosphors. Alternatively, such additional layers
24 may be deposited before the first phosphor deposition, or after removal of the first phosphor,
25 depending on their desired placement. A still further alternative is to deposit such additional
26 layers between the second and third phosphors. This photolithographic method allows for a
27 wide degree of flexibility.

28 The second phosphor layer, and any third phosphor or additional layers, are selectively
29 removed from the regions above the first phosphor by a lift-off step. Preferably a solvent
30 solution is used which is predominantly a polar, aprotic solvent, and which will allow removal
31 of the resist in a time which is sufficiently fast that it does not cause significant hydrolysis of
32 the phosphors. For lift-off of a zinc sulfide phosphor, a solution of a minor amount (up to

1 50%, preferably about 5 to 20%, most preferably about 10% by volume) of methanol in
2 toluene is particularly preferred. Other non-aqueous, polar, aprotic solvents such as
3 acetonitrile, diethyl carbonate, propylene carbonate, dimethyl ether, dimethyl formamide,
4 tetrahydrofuran and dimethyl sulfoxide might also be used, depending on the particular
5 phosphors involved. The particular solvents used are chosen to minimize hydrolysis of the
6 phosphors while still removing the resist in a reasonable time period.

7 This first layer of the patterned phosphors may then be covered by another layer of a
8 phosphor material which is the same as or different from the first, second, or third phosphors,
9 in order to achieve the desired threshold voltages and luminosities for the sub-pixel element.
10 Alternatively, the threshold voltages and the luminosities for the sub-pixel elements may be set
11 with appropriate threshold voltage adjustment layers deposited below, between or above the
12 phosphors. In addition, or as a further alternative, the thicknesses of the phosphor deposits
13 may be varied to equalize the threshold voltages and to set the desired relative luminosities of
14 the sub-pixel elements. A still further or additional alternative to the above is to adjust one or
15 more of the areas of the sub-pixel elements, or the compositions of the phosphors and dopants,
16 in order to achieve the desired threshold voltages and relative luminosities of the sub-pixel
17 elements.

18 The photolithographic method of this invention allows great flexibility in the
19 adjustment of the above parameters and/or layers in order to individually set the desired
20 threshold voltages and relative luminosities of the sub-pixels elements.

21 Above the patterned phosphor structure 30 may be formed a second dielectric layer 28
22 and a patterned transparent conductor to define column electrodes 24 perpendicular to the row
23 electrodes 14 positioned beneath the phosphor structure 30.

24 When $Zn_{1-x}Mg_xS:Mn$ is used as a phosphor, the value of x is preferably between about
25 0.1 and 0.3, more preferably between about 0.2 and 0.3. When $SrS:Ce$ is used as a phosphor,
26 it may be codoped with phosphorus.

27 **a) Factors Affecting Pixel Performance**

28 This section is included to provide guidance for the criteria relating to the choice of
29 phosphors and the particular thicknesses to be used in the sub-pixel elements. In the following
30 section, the thickness criteria are discussed for particular preferred, and exemplary phosphors.

31 A high pixel energy efficiency is required to obtain a high luminosity and a high
32 overall energy efficiency for an electroluminescent display. The pixel energy efficiency is

1 defined as the ratio of light power within the desired wavelength range radiated from the
2 surface of a pixel divided by the electrical power input to the pixel. The light power,
3 expressible in watts per square meter, can be directly related to the luminosity of the pixel
4 expressed in candelas per square meter using well known relationships. These relationships
5 are a function of the angular distribution of light from a sub-pixel as well as a wavelength
6 factor accounting for the sensitivity of the human eye to different colours or wavelengths of
7 light. The following discussion details the factors that affect the pixel energy efficiency. This
8 efficiency can be expressed as the product of several independent factors. These are defined
9 here as the electron injection efficiency, the electron multiplication efficiency, the activator
10 excitation efficiency, the radiative decay efficiency and the light extraction efficiency. Four of
11 these five factors are dependent on the thickness of the phosphor film as discussed below.

12 1. Electron Injection Efficiency

13 The electron injection efficiency is defined herein as the ratio of the energy flux of hot
14 electrons injected into the phosphor layer of a display sub-pixel to the electrical power input to
15 that sub-pixel. Generally, injection occurs by electrons tunnelling into the phosphor from
16 surface states at or near the interface between the phosphor and the immediately adjacent
17 dielectric layer. With reference to the numbers in Figure 9, typically, the energy of the
18 electrons in the surface states, shown at 32, lies below the bottom of the electron conduction
19 band in the phosphor material. When an electric potential is applied across the phosphor, the
20 conduction band bottom, shown at 34, decreases linearly with distance away from the
21 interface, shown at 36. The slope of this linear decrease is proportional to the applied
22 potential, and inversely proportional to the phosphor thickness. Tunnelling will occur if the
23 distance (shown as the tunneling distance 38), between the interface 36 and the first point at
24 which the bottom of the conduction band 34, is approximately equal to the energy of an
25 electron in a surface state 32, and is sufficiently small, generally of the order of a few
26 nanometers. This distance can be reduced to the point where tunnelling occurs by increasing
27 the potential across the phosphor layer or decreasing the phosphor thickness for a fixed
28 potential.

29 Not all of the injected electrons that are injected will be "hot" electrons. In general,
30 there will be a distribution of energies for the surface electrons that can be injected into the
31 phosphor layer. If the energy difference between a surface electron and the bottom of the
32 conduction band is too small, the electron will be injected into the phosphor with a low energy.

1 Low energy or "cold" electrons tend to interact strongly with the phosphor host material and
2 lose their energy without light being generated. Thus, the fraction of hot or light-generating
3 electrons is related to the energy distribution of surface electrons. The surface electron energy
4 distribution is a function of the phosphor and immediately adjacent dielectric materials used.
5 The electron injection model described above can be distorted by the presence of trapped
6 positive or negative charges within the phosphor layer that can produce deviations from the
7 assumed constant electric field across the phosphor. Nevertheless, the general principles for
8 optimizing the hot electron injection efficiency by selecting an appropriate phosphor thickness
9 remain the same.

10 For a defined potential across the phosphor layer the electron injection efficiency in
11 general should decrease as a function of phosphor thickness because the injection tunnelling
12 probability will decrease due to decreased electric field strength. The potential across a sub-
13 pixel is normally selected in terms of the voltage and current delivery capability of the
14 electronic circuitry used to operate the sub-pixel and the threshold voltage desired for sub-
15 pixel operation. The fraction of this voltage across the phosphor layer is a function of the
16 thickness and dielectric constant of the phosphor and of the dielectric layers used in
17 conjunction with the phosphor layer, as previously discussed. The injection efficiency
18 decreases when the tunnelling probability drops because a larger fraction of the power input to
19 the pixel is dissipated due to resistive and dielectric hysteresis losses in the dielectric layers of
20 the pixel as well as resistive loss in the conductors supplying electrical current to the sub-
21 pixel. These sources of loss can be minimized through the use of dielectric layers having a
22 high dielectric constant as discussed above.

23 2. Electron Multiplication Efficiency

24 The electron multiplication efficiency is defined here as the energy conversion
25 efficiency associated with the generation of a large number of hot electrons through the
26 electron multiplication process described below from a lesser flux of injected hot electrons

27 Electron multiplication depends on a phenomenon whereby an electron accelerated in
28 the phosphor host material in response to the applied electric field can cause a second electron
29 to be extracted from the valence band where it is immobile into the conduction band. The
30 second electron can then also be accelerated in response to the applied field. For this to occur,
31 the initial electron must have energy at least equal to twice the band gap energy above the top
32 of the valence band, shown at 40 in Figure 9. Electron multiplication is a cascading process

1 that can produce a large number of accelerating electrons from a few injected electrons. The
2 multiplication factor increases as the applied potential across the phosphor layer is increased.
3 For a fixed potential across the phosphor the electron multiplication efficiency should be
4 highest for relatively thin phosphor layers where the electric field strength is relatively high
5 and the distance electrons travel between multiplication events is relatively low. The reduced
6 distance of travel lowers the probability that the electrons will scatter from the phosphor host
7 crystal lattice so that they lose energy and fall out from the cascading process. Electron
8 multiplication is useful particularly if the density of injection electrons is relatively low.

9 The electron multiplication and charge injection processes will be affected by positive
10 charges (holes) created when electrons are promoted from the valence band to the conduction
11 band of the phosphor host material. These charges should be able to migrate in response to the
12 applied potential in the opposite direction, to the interface from which the initial electrons
13 were injected. Facilitation of this migration minimizes the buildup of charge within the
14 phosphor film that will tend to distort the electric field within the phosphor that is induced by
15 the applied potential. The hole-migration rate may be increased if the phosphor layer is
16 relatively thin and the driving electric field is relatively large.

17 3 Activator Excitation Efficiency

18 The activator excitation energy is defined here as the fraction of hot electrons that
19 cause an electron on activator atoms to be promoted to a more energetic or excited state.

20 The light emitting centers or activators in a phosphor are dopant atoms dispersed
21 throughout the host material, the electrons of which are promoted to an excited state when a
22 hot electron collides with them. The electrons in the excited atoms then can return to their
23 normal ground state, causing a photon to be emitted. The excitation process is called
24 activation. The luminosity of a phosphor is proportional to the rate at which photons are
25 generated. This rate is in turn proportional to the flux of hot electrons incident on the dopant
26 atoms, which is controlled by the factors discussed in the previous paragraphs. The efficiency
27 of the activation process is related to the cross section presented by the dopant atoms to the
28 incident hot electrons. This efficiency is mostly determined by the local environment of the
29 dopant atoms in the host material of the phosphor, and is not likely strongly affected by the
30 phosphor thickness.

31 4. Radiative Decay Efficiency

32 The radiative decay efficiency is defined herein as the fraction of excited dopant atoms

1 that decay to their ground state, emitting a photon with an appropriate energy to contribute to
2 sub-pixel luminosity.

3 When a dopant atom is activated, it can return to its initial or ground state by a variety
4 of processes, of which only some result in the generation of a photon contributing to the
5 phosphor luminosity. The photon must have an energy corresponding to the wavelength range
6 for the colour of light desired (red, green or blue) to be counted as effectively contributing to
7 the luminosity. One of the factors affecting the radiative decay efficiency is the local electric
8 field present at the dopant atom site. This in turn relates back to the phosphor thickness, as
9 well as to the total potential across the phosphor layer. In general, if the electric field strength
10 is too high, a process called field quenching occurs, whereby the excited electrons in the
11 dopant atom have an increased probability of being removed from that atom and injected into
12 the conduction band of the host material. The removed electrons eventually lose their energy
13 in a collision process that does not result in photon emission, resulting in a reduction in
14 radiative decay efficiency. The presence of a high, externally applied electric field at the
15 dopant atom site might also alter the wavelength of any emitted photons, moving it in or out of
16 the range where the photon contributes to the desired colour.

17 Generally, the radiative decay efficiency should be highest when the local electric field
18 strength is below the value at which field quenching can occur. For a fixed potential across
19 the phosphor layer, the field strength is reduced if the phosphor thickness is increased.

20 5. Light Extraction Efficiency

21 The light extraction efficiency is defined herein as the fraction of photons within the
22 required energy range to contribute to sub-pixel luminosity generated within the phosphor that
23 are transmitted through the front surface of a sub-pixel, thus directly contributing to useful
24 luminosity.

25 Not all of the light generated by activators within the phosphor material is extracted
26 from the phosphor layer to provide useful luminosity. Typically, some of the light generated
27 within the phosphor may reflect internally from the phosphor surfaces, or from any other
28 interface within the sub-pixel structure. There may be multiple reflections of this nature
29 before the light is transmitted through the upper surface of the sub-pixel structure thus
30 contributing to useful luminosity. The longer the optical path that the photons travel before
31 escaping the pixel structure, the greater is the probability that the light will be absorbed within
32 the sub-pixel structure, causing a reduced light extraction efficiency. Even if there are no

1 internal reflections, light may still be absorbed along the direct path between the activator
2 atoms from which the light originates and the outer surface of the phosphor. The probability
3 of absorption increases as the thickness of the phosphor layer is increased, so the light
4 extraction efficiency, from this standpoint, is decreased when the phosphor thickness is
5 increased. The probability of reflections (reflection coefficient) at the phosphor surfaces is
6 related to the difference in the index of refraction of the phosphor material and the adjacent
7 layers in the sub-pixel structure. This is an intrinsic property of the materials, and is not
8 dependent on thickness. However, if the phosphor thickness should become sufficiently thin as
9 compared to the wavelength of light in that material, then the reflection coefficient may have a
10 dependence on individual layer thickness within the phosphor and other layers that are part of
11 the sub-pixel structure. Any such dependence is not readily predictable from theory, but can be
12 experimentally determined.

13 **6. Total Pixel Energy Efficiency**

14 The total pixel energy efficiency is the product of the five efficiency factors defined
15 and described in the preceding paragraphs. For some of these factors, efficiency is an
16 increasing function of phosphor layer thickness, and for others it is a decreasing function of
17 phosphor thickness. Achieving an overall efficiency optimization is a complex process
18 involving many parameters, and in the end the optimum thickness of individual phosphors in a
19 sub-pixel structure may be determined experimentally, using the considerations discussed
20 above as a guide. Typically, the pixel energy efficiency will have a maximum as a function of
21 phosphor thickness due to the trade off between the five contributing factors. The shape of
22 this efficiency curve is dependent on many parameters, and the overall optimum phosphor
23 thickness and operating voltage to achieve maximum luminosity and electro-optic efficiency
24 can be determined experimentally, using the scientific principles discussed above as a guide.

25 **b) Criteria for Selecting Phosphor Deposit or Threshold Voltage Adjustment Layer**

26 **Thicknesses and Areas of Sub-pixels**

27 The performance of a pixel employing a patterned phosphor structure can be optimized
28 through a judicious choice of design parameters. These parameters include the compositions
29 of the phosphors and the dopant concentrations, the relative areas of the sub-pixels and the
30 thickness of the phosphor deposits and any additional threshold voltage adjustment deposits of
31 dielectric or semiconductor materials incorporated into one or more of the sub-pixel elements
32 for the purpose of ensuring that the relative luminosities of the sub-pixel elements bear set

1 ratios to one another at each modulation voltage used, to enable colour balance control for a
2 pixel by setting the colour coordinates for the sub-pixels, most preferably enabling gray scale
3 capability, for full colour. Optimum parameters can be selected by following the steps
4 outlined below:

- 5 1. Select the sub-pixel areas, choosing between:
- 6 i. Equal areas for each sub-pixel
7 ii. Equal areas for each sub-pixel, but including more than one sub-pixel for one
8 or two of the three colours
9 iii. Variable areas selected to maximize total luminosity with the required colour
10 balance, but constrained to a value between a minimum and a maximum width.
11 iv. Variable areas for each sub-pixel and more than one sub-pixel for one or two of
12 the three colours.

13 The selection of the preferred options is on the basis of a trade-off between achieving
14 the maximum possible luminosity, achieving the desired colour coordinates for the sub-pixels
15 using appropriate red, green and blue filters, achieving gray scale operation, avoiding
16 difficulties with uneven electrical loading of the row and column drivers and ease of
17 fabrication considerations. The selection of more than one sub-pixel for a single colour rather
18 than a single sub-pixel with increased area is governed by a desire to keep the load impedance
19 seen by row or column drivers above a critical value below which the luminosity of some sub-
20 pixels may be lower than intended due to a voltage drop caused by excessive current flow from
21 the driver. In this situation, gray scale fidelity may be impaired and undesirable image
22 artifacts may be created. If the load impedance of a set of sub-pixels driven by one driver is
23 too low, the load can be shared by more than one driver by selecting more than one sub-pixel
24 per colour. Independently addressable sub-pixels within a single pixel can be created by
25 incorporating one or more rows and one or more columns within the pixel. One possible sub-
26 pixel arrangement is a "quad-pixel" containing four pixels defined by the intersection of each
27 of two columns and two rows. In this arrangement, two of the pixels can be assigned to one
28 colour.

29 2. Determine the phosphor deposit thicknesses for the performance limiting sub-pixel
30 using the steps given below. These steps are independent of the choice of sub-pixel options i.
31 to iv. above.

32 A. Determine the optimum threshold and total driving voltages for the pixel. This

choice is governed by considerations of the available driver electronics, the desired sub-pixel luminosities and the desired energy efficiency. Generally, the highest feasible threshold and total voltage will give the highest luminosity. Typically, threshold voltages of up to 200 V and modulation voltages up to 60 V can be provided, giving a maximum operating voltage of about 260 V. It is desirable that the threshold voltage for all sub-pixels be equal so that the maximum threshold voltage can be applied to the rows, consistent with having no emission from any pixel when zero modulation voltage is applied. This facilitates full gray scale control and minimizes overall power consumption as discussed above.

B. Determine a thickness of each phosphor deposit to be used for each sub-pixel that will give the desired threshold voltage, consistent with providing the desired colour coordinates and luminosity. In one embodiment of this invention a two layer phosphor structure is used (see Example 2). There, it is found experimentally that a deposit of SrS:Ce, with 0.1% Ce dopant, with a thickness between about 1.4 and 1.8 μm is appropriate for the blue sub-pixel for the voltages given above. Co-doping of this phosphor with phosphorous to provide charge compensation for the cerium may have the effect of increasing the threshold voltage by about 25%. Two layers of phosphor deposits comprising about 0.7 to 0.9 μm of SrS:Ce and about 0.35 to 0.45 μm of ZnS:Mn are appropriate for the red and green sub-pixels at similar voltages. The correct colour coordinates can be achieved through the use of appropriate filters for red and green. In other embodiments, a single layer of patterned phosphor deposits is used. In Example 3, it is found experimentally that an SrS:Ce deposit of 1.2 to 1.4 μm is appropriate for the blue sub-pixels, while a deposit of $\text{Zn}_{1-x}\text{Mg}_x\text{S}:Mn$ of 0.3 to 0.5 μm is appropriate for the green and red sub-pixels. In Example 4, the red and green sub-pixels can be formed from three stacked phosphor deposits of 0.4 to 0.6 μm of $\text{Zn}_{1-x}\text{Mg}_x\text{S}:Mn$ sandwiched between two 0.08 to 0.1 μm layers of ZnS:Mn. In Example 5, a deposit of 1.2 to 1.4 μm of SrS:Ce can provide both the green and blue sub-pixels, while a 0.4 to 0.5 μm deposit of ZnS:Mn can provide the red sub-pixels. In the foregoing, the suggested compositions and thickness ranges are dependent on the physical and

- 1 electroluminescent properties of the phosphor layers, as well as on the electrical
2 characteristics of the threshold voltage adjustment layers and any additional
3 dielectric layers, and so variations may be expected, depending on the specific
4 properties of the materials employed.
- 5 C. Identify which of the sub-pixels defined above will have the lowest luminosity
6 relative to the required luminosity to give the desired pixel colour balance. The
7 thickness of each phosphor deposit for this sub-pixel is then selected to be that
8 determined for this sub-pixel in step B.
- 9 3. Determine the area of the remaining sub-pixels and the thickness of their phosphor and
10 other threshold voltage adjustment layers. If the option of equal sub-pixel areas has been
11 selected, steps D and E should be followed. If equal areas and more than one sub-pixel for at
12 least one colour is selected, steps J and K should be followed, provided that the sub-pixel
13 dimensions determined fall between the specified minimum and maximum values. If variable
14 areas have been selected using steps J and K , and the dimensions do not fall between the
15 specified minimum and maximum values, steps L and P should be followed instead.
- 16 D. find the thickness of each of the phosphor deposits for each remaining sub-
17 pixel that gives the desired colour coordinates and the desired luminosity
18 relative to the performance limiting sub-pixel. The threshold voltages for these
19 sub-pixels should in general be lower than that for the performance limiting
20 sub-pixel.
- 21 E. Determine the thickness of a dielectric or semi-conductor deposit required for
22 increasing the threshold voltage for these sub-pixels to the threshold voltage of
23 the performance limiting sub-pixel. This deposit can be disposed under, over,
24 or in the case where more than one phosphor deposit is employed, between
25 phosphor deposits, with the order of the deposits selected on the basis of ease of
26 fabrication considerations, or on the basis of physically isolating incompatible
27 deposits from one another.
- 28 F. Decide which colours will have more than one sub-pixel. This will typically
29 be the performance-limiting colour.
- 30 G. With the increased number of sub-pixels for the original performance limiting
31 colour, re-assess which colour is the performance limiting one, and select the
32 thickness of its phosphor deposits as outlined in step B.

- 1 H. Determine the thickness of the phosphor deposits for the remaining sub-pixels
2 to give the desired luminosities relative to the performance limiting sub-pixel.
- 3 I. Determine the thickness of a threshold voltage adjustment layer required to
4 increase the threshold voltage of the remaining sub-pixels relative to that of the
5 performance limiting sub-pixel.
- 6 J. Select the thickness of all phosphors to make their threshold voltage equal with
7 reference to steps B and C.
- 8 K. Adjust the sub-pixel areas to achieve the desired relative luminosities.
- 9 L. Calculate the sub-pixel areas to achieve the desired relative luminosities.
- 10 M. Determine which areas require dimensions outside of the specified range, and
11 adjust them up or down accordingly.
- 12 N. Taking into account the adjusted sub-pixel areas, reevaluate which colour is the
13 performance limiting colour, and select the thickness for each of its phosphor
14 deposits as determined in step B.
- 15 O. Select the thickness of the remaining sub-pixels to achieve the desired relative
16 luminosities.
- 17 P. Select a dielectric or semiconductor deposit to adjust the threshold voltages of
18 the remaining sub-pixels to that of the performance limiting sub-pixels as in
19 step E.

20 **c) Exemplary Application of Selection Criteria**

21 Application of the above selection criteria is shown below for a two layer phosphor
22 structure in which the threshold voltage and luminosities are set by a layer of SrS:Ce above a
23 patterned layer of SrS:Ce and ZnS:Mn.

24 **1. Total SrS:Ce Thickness**

25 The combined thickness of the SrS:Ce layers on the blue sub-pixel is determined on
26 the basis of the desired threshold voltage for the display. This is in turn dictated by the row
27 and maximum column voltages and concomitant currents for full luminosity that can be
28 provided by the display driver electronics. Typically, row drivers can provide a maximum 200
29 V output for the threshold voltage and column drivers can provide a maximum 60 V
30 modulation voltage. It is found experimentally that a 0.1% cerium doped strontium sulfide
31 layer with a thickness between about 1.4 and 1.8 microns is appropriate for these voltages. In
32 some cases the strontium sulfide is co-doped with phosphorus in the same molar proportion as

cerium to provide charge compensation. Charge compensation may be provided because, relative to the host atomic species, cerium is deficient one electron per cerium atom. Phosphorus has one excess electron per phosphorus atom and can compensate for the missing electron from the cerium. Phosphorus induced charge compensation is thought to inhibit spontaneous charge compensation through the creation of atomic vacancies that can change the properties of the phosphor, and possibly reduce the electroluminescent efficiency of the phosphor. Phosphorus co-doping may have the effect of increasing the threshold voltage by about 25% and so this difference must be taken into account in establishing the strontium sulfide layer thickness.

2. The ZnS:Mn Thickness

The ZnS:Mn layer thickness on the red and green pixels is determined on the basis of providing the correct red to green to blue luminosity ratio of 3:6:1 at full luminosity. Generally, the limiting luminosity from ZnS:Mn is the green luminosity. The patterned phosphor structure of this invention makes use of the combined green emission from the ZnS:Mn and the SrS:Ce covering the green sub-pixel. Accordingly, the ZnS:Mn thickness is determined from the required blue to green ratio of 1:6 at the total applied voltage (sum of the threshold and modulation voltage) for full luminosity. The green emission is also dependent on the thickness of the second SrS:Ce layer overlying the green sub-pixel, so the thickness of this layer is dependent on the choice of the thickness of the first SrS:Ce layer as discussed below. The net green luminosity is also dependent on the optical absorption in the filter used to obtain satisfactory colour coordinates for the green pixel. Accordingly, some experimental optimization is required to select the ZnS:Mn thickness. For the total applied voltage in this example, a ZnS:Mn layer thickness in the range of 0.35 to 0.45 μm is satisfactory. The correct red luminosity can be obtained by selecting an appropriately attenuating red filter.

3. The First SrS:Ce Layer Thickness

The thickness of the first SrS:Ce layer is chosen to match the threshold voltage for the three sub-pixels and thus depends on the ZnS:Mn thickness chosen above. It is desirable that the threshold voltages be equal so that the maximum threshold voltage can be applied to the rows, consistent with having no emission from any pixel when zero modulation voltage is applied. This facilitates full gray scale control and minimizes overall power consumption as discussed above. The optimum thickness for the first SrS:Ce layer is in the range of about 0.7 to 0.9 for this example. In all of the foregoing, the specified ranges are dependent on the

1 physical and electroluminescent properties of the phosphor layers, as well as on the electrical
2 characteristics of the encapsulating dielectric layers, and so variations may be expected,
3 depending on the specific properties of the materials employed.

4 **d) Patterned Phosphor Fabrication Process**

5 The patterned phosphor structure 30 is described below in Examples 2 - 5, with
6 reference to preferred materials and conditions, to fabricate a pixel having red, green and blue
7 sub-pixels phosphor elements 30a, 30b, and 30c with component red, green and blue colours.
8 The process and structure are not limited by these examples, but are amenable to the
9 fabrication of EL displays with different construction and having a wide variety of pixel sizes,
10 ranges of pixel counts, and types of phosphors. The patterned phosphor structure is described
11 in combination with preferred thick film dielectric layers, phosphors, threshold voltage
12 adjustment layers, barrier diffusion layers, and injection layers, as described above.

13 The present invention is further illustrated by the following non-limiting examples.

14 **Examples**

15 **Example 1 - Isostatically Pressed Thick Film Dielectric Layer**

16 A first layer of Heraeus CL90-7239 (Heraeus Cermalloy, Conshohocken, PA) high
17 dielectric constant paste was screen printed using a 250 mesh screen having a 1.6 μm wire
18 diameter. The high dielectric constant material in the paste was PMN-PT. The printed paste
19 was dried for between 30 and 60 minutes at 150°C, with the longer times for a more heavily
20 loaded oven. A second layer of the same material was printed over the baked first layer and
21 then baked in at 300°C for 30 min. The thickness of the combined layers at this point was
22 about 26 μm . The entire structure was next cold isostatically pressed (CIPped) using a cold
23 isostatic press at 350,000 kPa (50,000 psi). To ensure adequate pressing and to develop a
24 relatively smooth surface on the dielectric layer, a sheet of aluminized polyester, with the
25 aluminized surface in contact with the dielectric, was laid over the dielectric surface. A
26 further two sheets of plastic bagging material were then folded around the part, so as to isolate
27 the part from an outer, compliant sealing bag to prevent the sealing bag from tearing. The
28 sealing bag was evacuated of air and hot sealed. The bag was isostatically pressed at the
29 indicated pressure and held at that pressure for no more than 60 seconds. After pressing the
30 part was removed from the bag and fired in a belt furnace using a typical thick film
31 temperature profile with a peak temperature of 850°C. After pressing and firing the dielectric
32 material was essentially non-porous. The thickness of the dielectric layer at this point was in

1 the range of 15 - 20 μm , typically 16 μm .

2 To test the compressed thick film dielectric layer, it was fashioned into a capacitor
3 between 1 cm^2 metal electrodes evaporated onto its surface. An AC, 60 Hz signal was applied
4 until dielectric breakdown was observed. Testing six samples, gave the following results in
5 Table 1.

6 Table 1: Improved Dielectric Properties of Isostatically Pressed Thick Film Dielectric Layer

	Dielectric Thickness	Capacitance/cm ² @ 1 kHz	Breakdown Voltage
UnCIPped	24 μm	0.120 $\mu\text{F}/\text{cm}^2$	80 - 90 V
CIPped	16 μm	0.156 $\mu\text{F}/\text{cm}^2$	140 - 160 V

10
11 Based on the above data, using a dielectric constant of 3300 for the unCIPped material,
12 the dielectric strength is roughly calculated as 3×10^6 V/m. Using a dielectric constant of
13 2800 for the CIPped material, the dielectric strength is roughly calculated as 10^7 V/m.

14 To further smooth the surface of the dielectric layer, a second dielectric layer
15 comprising lead zirconium titanate was applied using sol gel precursor materials, as described
16 in Example 3 of U.S. Patent 5,432,015. The thickness of this sol gel layer was about 2 μm .

17 Example 2 - Two Layer Patterned Phosphor Structure

18 Reference may be had to Figure 6 for the EL laminate of this example.

19 2.1. Thick Film Substrate Layers

20 The purpose of the thick film substrate is to provide a mechanical support, a first pixel
21 electrode, and a thick film dielectric layer to electrically isolate the electrode from the
22 phosphor structure. The electrical isolation is required to provide a means to control the
23 density of current over a large area of pixels. The current control results from the injection of
24 localized charge into the phosphor structure from the vicinity of the interface between the
25 phosphor and a dielectric material in contact with it, rather than from the electrode itself. The
26 dielectric layer has a high dielectric constant to minimize the voltage drop across it when a
27 voltage is applied between the pixel electrodes, and a dielectric strength sufficient to prevent
28 an electric breakdown of the dielectric when an appropriate voltage is applied between the
29 pixel electrodes. The teachings of U.S. Patent 5,432,015 to Wu et al., describing the thick film
30 substrate in greater detail are incorporated herein by reference.

31 a) Rear Ceramic Substrate and Rear Electrode

1 The rear substrate was a 0.63 mm thick 96% purity alumina sheet (Coors Ceramics,
2 Grand Junction, Colorado, USA). This material typically is used for the fabrication of thick
3 film hybrid electronic circuits. A $0.3 \mu\text{m}$ thick gold electrode with provision for making an
4 electrical contact as shown in Figure 5 was first deposited on the alumina substrate. The
5 alumina was unpolished to provide sufficient surface roughness to facilitate an adequate
6 bonding strength for the gold layer. The gold electrode was screen printed using Heraeus RP
7 20003/237 - 22% organometallic paste (Heraeus Cermalloy) to form row electrodes and then
8 fired at 850°C using standard manufacturers thick film methods to form the finished gold film.

9 b) Thick Film Dielectric Layers

10 The next step was to apply a thick film dielectric layer. This layer was fabricated in
11 two individual layers, a screen printed and isostatically pressed dielectric layer, and a
12 smoothing sol gel layer, as set out in Example 1. The thick film dielectric layer had a fired
13 thickness of $15 - 20 \mu\text{m}$, while the sol gel layer had a thickness of about 2μ .

14 2.2. Diffusion Barrier Layer

15 A 300 \AA alumina layer was e-beam evaporated onto the surface of the lead zirconium
16 titanate layer. The alumina film was deposited with the substrate at 150°C and the deposition
17 rate was 2 \AA/sec . The purpose of this layer was to prevent diffusion of atomic species in the
18 thick film dielectric into the phosphor layer.

19 2.3. Injection Layer

20 A 100 \AA hafnia layer was e-beam deposited onto the alumina diffusion barrier layer.
21 The hafnia layer was deposited with the substrate at 150°C and was deposited at a rate of 1
22 \AA/sec .

23 2.4. Patterned Phosphor Structure

24 a) First SrS:Ce Layer

25 A first SrS:Ce layer was deposited with a thickness in the range of $0.70 - 0.95 \mu\text{m}$.
26 The SrS powder used for the evaporation source was made by the process of this invention
27 described below. The SrS was doped with 0.1% Ce by mixing the appropriate amount of CeF_3
28 into the evaporation source material. The deposition was done by reactive evaporation, with
29 the substrate temperature at 450°C and the deposition rate at 30 \AA/sec . An H_2S atmosphere at
30 a pressure of 0.01 Pa (0.1 mT) was maintained in the vacuum chamber during the deposition,
31 sufficient to prevent a deficiency of sulphur as compared to the stoichiometric ratio in the
32 deposited film. Following deposition, some of the parts were annealed at 600°C in a vacuum

1 for 45 min. to anneal the SrS:Ce layer. The annealed parts developed a web of micro-cracks in
2 the thin film layers following the annealing, but showed somewhat higher initial luminosity in
3 final testing, as described below.

4 b) Patterning of SrS:Ce Layer

5 Following deposition, the initial SrS:Ce layer was patterned using photo-lithographic
6 processes. A negative polyisoprene-based photoresist material, OMR 83 available from the
7 AZ Photoresist Products division of Hoechst Celanese Corp., Somerville N.J., was employed
8 to protect the SrS:Ce on the blue sub-pixels during the etching process used for patterning.
9 The viscosity of the resist was 500 centipoise and spun onto the parts at 1700 rpm for 40 sec.
10 The viscosity was chosen to ensure that the relatively rough surface (as compared to
11 semiconductor surfaces) was adequately covered by the resist and to optimize a subsequent lift
12 off step set out below. The final resist thickness was in the range of 3.5 to 4.0 μm .
13 The resist was exposed through a patterning mask designed to allow exposure of the resist
14 over the area corresponding to the blue sub-pixel elements.

15 Following exposure, the resist was developed by spraying on developer solution at
16 while spinning the part at 1000 rpm for 30 sec. The Developer was OMR B from the AZ
17 Photoresist Products division of Hoechst Celanese Corp., Somerville, N.J. Following
18 application of the developer, a 50:50 mixture of developer and OMR Rinse solution were
19 sprayed on for 10 sec, followed by an application of rinse only, for 30 sec, all while spinning
20 the substrate at 1000 rpm. Following rinsing, the part was de-scummed in an oxygen plasma
21 etcher for 2 min.

22 Following rinsing of the resist, the part was immersed in anhydrous methanol for 1
23 min. to allow any pores in the surface to be filled with fluid. The part was then immersed at
24 ambient temperature in a solution of 0.5% concentrated hydrochloric acid in anhydrous
25 methanol for 45 - 70 sec to dissolve the SrS:Ce from the red and green sub-pixels element
26 areas. The etching reaction entails reaction of the hydrochloric acid with SrS:Ce to form
27 hydrates of strontium chloride, which is soluble in methanol. The time to etch is dependent on
28 the thickness of the SrS:Ce layer to be dissolved. The pre-immersion in pure anhydrous
29 methanol was designed to inhibit hydrochloric acid from penetrating into the pores and
30 causing deleterious etching or contamination of the underlying structure. Following etching,
31 the substrates were rinsed in methanol for 2 min. and dried under a nitrogen flow. The etching
32 solution did not dissolve the underlying hafnia injection layer material.

1 c) ZnS:Mn Deposition

2 Following etching of the initial SrS:Ce layer, a layer of ZnS:Mn was e-beam
3 evaporated onto the part to provide the red and green phosphor sub-pixel elements. The Mn
4 concentration was 0.8% and the layer thickness was in the range of 0.3 to 0.5 μm . The
5 substrate temperature during deposition was 150°C and the deposition rate was 20 Å/sec.

6 d) Hafnia Injection Layer

7 This layer was provided as an interlayer to inhibit interdiffusion of dopant species
8 between the SrS and ZnS phosphors, and at the same time preserve good electron injection
9 conditions. The layer may not be needed, provided that good quality phosphor films are
10 deposited. The layer was e-beam evaporated to a thickness of 300 Å with a substrate
11 temperature of 150°C and a deposition rate of 1 Å/sec.

12 e) ZnS:Mn Lift-Off

13 In this step, the hafnia interlayer and the underlying ZnS phosphor were removed in the
14 positions where they overlay the blue sub-pixels. This lift-off process was performed by
15 dissolving the resist layer that remained over the blue sub-pixels during the ZnS:Mn and
16 hafnia depositions. To initiate the lift-off process, the part was immersed in a mixture of 10%
17 by vol. methanol in toluene at ambient temperature for 20 to 40 min. The part was removed
18 from the solvent and wiped off, then rinsed in isopropyl alcohol for two more minutes, and
19 dried using a nitrogen gas stream.

20 f) Second SrS:Ce Layer

21 A second SrS:Ce layer with a thickness of 0.8 - 0.9 μm was deposited over the entire
22 pixel area. The deposition was done under the same conditions as for the first SrS:Ce layer.
23 The resulting phosphor structure now consisted of a 1.6 μm thick SrS:Ce film for the blue sub-
24 pixels (widths 150 μm) and, for the red and green sub-pixels (combined width 300 μm), a 0.4
25 μm thick layer of ZnS:Mn covered with a thin hafnia injection layer and a 0.8 μm thick SrS:Ce
26 layer.

27 2.5. Second Injection Layer

28 A second 100 Å thick hafnia injection layer was deposited on top of the completed
29 pixels (now the patterned phosphor structure) using the same deposition conditions used for
30 the first injection layer. As for the first injection layer, the second injection layer was omitted
31 for some of the samples.

32 2.6. Second Diffusion Barrier Layer

1 A second 300 Å thick diffusion barrier layer was deposited on top of the second
2 injection layer using the same procedure as for the first diffusion barrier layer.

3 **2.7. Annealing**

4 For some samples, the entire substrate was then annealed in air for 10 min. at 550°C.
5 The benefits and difficulties with cracking were similar as for annealing at the earlier stage.

6 **2.8. Transparent Electrode Layer**

7 A second resist layer was applied to the substrate using the same procedure as outlined
8 above for the SrS:Ce layer, but using a photo-mask so as to place a resist layer in those
9 locations that were not to be covered by the transparent electrode material. This entailed
10 exposing the resist between those areas (shown in Figure 5) to be covered by the transparent
11 electrodes for each sub-pixel element 30a, 30b, and 30c. The transparent electrodes were
12 designed for external connection for testing of the pixel.

13 An indium tin oxide layer with a thickness in the range of 3000 to 6000 Å was e-beam
14 evaporated over the resist layer. The part was held at 250 to 350°C during the deposition
15 process. The deposition rate was 2 Å/sec. Alternatively, the indium tin oxide film could be
16 deposited using sputtering. Following the deposition, the superfluous indium tin oxide was
17 lifted off using the same process as used for lift off of the ZnS:Mn layer. Again, lift off was
18 accomplished by dissolution of the resist layer under the indium tin oxide from the step edges.
19 Next, the processed part was heated at 550°C in air and held at that temperature for 10 min.,
20 cooled and then heated in nitrogen at 550°C for a further 5 min. to anneal the indium tin oxide
21 layer to lower its electrical resistance. The ITO lines so formed were about 130 µm wide, with
22 20 µm spacings.

23 **2.9. Metal Contact Deposition**

24 To make contact to the transparent conductors, a silver-based polymer thick film
25 (Heraeus PC 5915) was deposited to make contact with the indium tin oxide electrodes. The
26 conductor was printed beyond the edge of the pixel to a contact pad. The conductor paste was
27 cured at 150°C for about 30 minutes.

28 **2.10. Filter Plate Attachment and Sealing**

29 The pixel structure was overlaid with a glass cover sheet sealed to the pixel structure
30 using an epoxy perimeter seal. The glass sheet had polymer filter film (Brewer Science)
31 deposited on the side of the glass facing the pixel structure aligned with the red, green, and
32 blue sub-pixel elements with the thickness of the polymer films adjusted to give appropriate

1 colour coordinates for the respective sub-pixels. A small hole had been laser drilled through
2 the bare alumina substrate prior to processing to provide a gas path between the rear of the
3 substrate and the void between the front of the pixel structure and the cover plate. A ceramic
4 pot filled with molecular sieve desiccant was sealed to the rear of the substrate aligned over
5 the hole. The ceramic pot and the void space were evacuated through a hole in the pot and this
6 hole was then sealed with a polymer bead (ex. curable epoxy bead). Sufficient desiccant was
7 provided to absorb any moisture that may have accumulated in the pixel structure during
8 processing and that may have leaked through the seals over time. This facilitated the
9 accumulation of luminosity data over time without device degradation caused by exposure of
10 the internal pixel structure to moisture or other atmospheric contaminants.

11 2.11. Test Results

12 Several pixel structure devices were built as described above and tested at ambient
13 temperature with repetitive alternating positive and negative voltage pulses 85 microseconds
14 long and 60 volts above the threshold voltage in amplitude on all three sub-pixels. The
15 repetition rate was 180 pulses per second. Under these operating conditions, the average
16 luminosity, as measured through the filter plates, was in the range 80 - 120 candelas per square
17 meter. The average colour coordinates fell within the range 0.39< x <0.42 and 0.38< y <0.42.
18 The threshold voltage for each sub-pixel was in the range of 120 to 150 volts.

19 The patterned phosphor structure of this example was also compared to the
20 performance of an EL laminate prepared as in Example 2, but using conventional colour by
21 white phosphor layers as shown schematically in Figure 1. The SrS:Ce layer was 1 μm thick,
22 while the ZnS:Mn layer was 0.3 μm thick. All other layers in the EL laminate were as
23 disclosed above in this example, including a hafnia injection layer between the phosphor
24 layers. Figures 3 and 4 show the luminosity vs. voltage curves for these two displays, Figure 3
25 showing unfiltered luminosity and Figure 4 showing filtered luminosity. As seen in the
26 Figures, when threshold voltages are taken into account, the unfiltered luminosity was
27 generally improved with the patterned phosphor structure of the present invention. The two
28 displays had a very similar L₄₀ (luminosity at 40 V above the threshold voltage), but at higher
29 voltages the patterned phosphor structure display was 50% more luminous than the L₆₀
30 (luminosity at 60V above the threshold voltage) of the colour by white display. However, the
31 patterned phosphor structure display looks much different than conventional colour by white
32 in that it is composed of alternating columns of blue and yellow-white. Since its light output

1 is somewhat tailored to the filter above it, it is the filtered luminosity which is more important.

2 When differences in threshold voltages are accounted for between the two displays,
3 Figure 4 shows that the filtered luminosity for the patterned phosphor structure of Example 2
4 is generally about twice that of the colour by white display. The difference at L40 is 100%,
5 and at L60, the difference is 110%.

6 **Example 3 - Single Layer Phosphor Structure**

7 This variant of the patterned phosphor structure requires only a single SrS:Ce
8 deposition and includes in the same layer, a manganese doped zinc magnesium sulfide for the
9 red and green sub-pixel elements. For $Zn_{1-x}Mg_xS:Mn$, the value of x was in the range from 0.1
10 to 0.3. This phosphor has a much stronger green emission than ZnS:Mn, and can provide
11 adequate green emission without the use of a double layer structure employing SrS and ZnS
12 phosphors. The fabrication was as follows:

13 **3.1. Thick Film Substrate**

14 The substrate for this example was a 1.02 mm thick alumina sheet of approximate
15 dimensions 12 x 15 inches upon which a set of 480 gold conductor strips were printed using
16 Heraeus RP 20003/237 - 22% organometallic paste obtained from Heraeus Cermalloy and
17 fired to form the addressing rows of a VGA format 17 inch diagonal display. The center-to-
18 center spacing of the fired gold rows was 540 μm , the width of the rows was 500 μm and the
19 length of the rows was about 27 mm (10.5 inches). A composite thick film dielectric layer of
20 dimensions 26 x 35 cm (10.2 x 13.6 inches) was deposited on top of the addressing rows so as
21 to leave the ends of the rows exposed for forming electrical contacts using the methods similar
22 to those set out in Example 1. The high dielectric constant paste in this example was prepared
23 from ink concentrate 98-42 supplied by MRA Laboratories Inc. (North Adams, Massachusetts,
24 U.S.A.) prepared using high dielectric constant powder comprising PMN-PT. The concentrate
25 was mixed in a blender for 15 min. and then mixed with a solution of α -terpineol, ethyl
26 cellulose and oleic acid in the weight ratio of 100:30:1. The proportion of concentrate to
27 solution was 100:12 by weight. The resulting paste was vacuum filtered through a 10 μm
28 nylon filter and degassed in vacuum for a few minutes. The paste was deposited, CIPped and
29 fired using the methods set out in Example 1, except that the paste was sequentially printed
30 and baked three times prior to CIPping. The thickness of the resulting high dielectric constant
31 layer after CIPping was in the range of 15 - 20 μm . As in Example 1, a 2 μm thick layer of
32 lead zirconium titanate was then applied using sol gel precursor materials.

1 3.2. Diffusion Barrier Layer

2 The barrier layer consisted of 800 Å of alumina, deposited as in Example 2.

3 3.3. SrS:Ce Layer

4 A 1.2 to 1.4 μm thick layer of SrS:Ce co-doped with phosphorus was deposited using
5 e-beam evaporation using the method as set out in Example 2. The phosphor material was
6 prepared as set out in the strontium sulfide synthesis section (f) below, except that the
7 strontium carbonate powder was pre-doped with cerium and phosphorus to yield a strontium
8 sulfide phosphor material containing about 0.1 atomic percent cerium and about 0.15 atomic
9 percent phosphorus. The powder was fired without the addition of other powders, using the
10 temporal temperature profile and sulfur doped process gas as described in section (f) below.

11 3.4. SrS:Ce Patterning

12 The SrS:Ce layer was removed from the green and red sub-pixel element areas using
13 the same procedures as for Example 2, with the exception that the etching time was increased
14 to 1 - 4 min. to account for the thicker SrS:Ce layer. The remaining SrS:Ce stripes were about
15 190 μm wide with a spacing between the stripes of 350 μm .

16 3.5. Zinc Magnesium Sulfide Phosphor ($\text{Zn}_{1-x}\text{Mg}_x\text{S}: \text{Mn}$)

17 A 3000 to 5000 Å thick zinc magnesium sulfide film doped with manganese was
18 deposited using e-beam evaporation of ZnS doped with Mn and thermal co-evaporation of
19 magnesium metal. The relative evaporation rates for the ZnS and Mg were adjusted so as to
20 give a film with a Mg to Zn ratio of about 30:70. The deposition conditions and amount of
21 dopant were similar to those of Example 2 for deposition of ZnS:Mn. An alternative to the
22 manganese doped $\text{Zn}_{1-x}\text{Mg}_x\text{S}: \text{Mn}$ phosphor layer in this example is a double phosphor layer
23 comprising ZnS:Tb and ZnS:Mn, preferably with a diffusion barrier interlayer between them.

24 3.6. Threshold Voltage Adjustment Layer

25 A 1000 to 3000 Å alumina third dielectric layer was evaporated onto the pixel structure
26 with the thickness chosen to equalize the threshold voltages between the red, green and blue
27 sub-pixels. The deposition conditions were similar to those used for alumina deposition in
28 Example 2. In this example, this threshold voltage layer was only needed over the red and
29 green sub-pixel elements, so was subsequently removed from the blue sub-pixel elements in
30 the next lift off step.

31 3.7. Zinc-Magnesium Sulfide Lift-Off

32 A lift off process similar to that used in Example 2 for ZnS:Mn was used to dissolve

1 the resist covering the SrS:Ce on the blue sub-pixel elements. The dissolving time for lift-off
2 was about 45 min. The substrate was wiped off, rinsed in clean methanol for 30 sec. and spin-
3 dried for a further 30 sec. following etching. The result was removal of the (ZnMgS):Mn and
4 overlying alumina layer from the blue sub-pixel elements.

5 **3.8. Diffusion Barrier Layer Deposition**

6 An 800 Å thick layer of alumina was deposited, as in Example 2.

7 **3.9. Phosphor Annealing**

8 Optionally, the phosphor structure can was annealed at this stage in a belt furnace in air
9 for 10 min. at a peak temperature of 550°C.

10 **3.10. Transparent Electrode Fabrication**

11 This step to deposit and pattern column electrodes onto the display was carried out
12 using the methods as set out in Example 2, except that the surface of the processed part was
13 de-scummed using an oxygen plasma following the lift-off step and the part was annealed at
14 450°C for 5 min. in air for 5 min. rather than at 550°C for 10 min. following the de-scumming
15 process. The center-to-center spacing of the columns was 180 µm and the width of the
16 columns was 140 µm. The columns were aligned over the patterned sub-pixels. The column
17 length was 26 cm (10.2 inches) so that the columns extended over all of the rows.

18 **3.11. Metal Contact Deposition**

19 Sputtered silver metal contacts were fabricated to make contact to the display
20 assembly. For testing purposes, 20 adjacent rows were connected in parallel and 60 adjacent
21 columns were connected in parallel so as to allow illumination of a small square on the display
22 assembly suitable for luminosity and colour coordinate measurements.

23 **3.12. Filter Plate Attachment and Sealing**

24 These steps were as performed for Example 2.

25 **3.13. Test Results.**

26 Several 17 inch diagonal displays were fabricated and tested as described above. The
27 threshold voltage for the blue pixels was in the range of 130 - 160 volts. The threshold voltage
28 for the red and green pixels was in the range 130 - 140 volts. When red, green and blue filters
29 were disposed in front of the corresponding sub-pixels, it was found that a threshold voltage of
30 140 volts could be used to achieve a minium luminosity below 1 cd/m² for all of the pixels.
31 The luminosity range for the combined sub-pixels with the filters in place was 35 - 60 cd/m²
32 for 40 volts above the threshold voltage and a refresh rate of 120 Hz. The driving pulses were

1 260 microseconds in duration. The corresponding colour coordinates for the combined sub-
2 pixels were in the range of 0.43 - 0.46 for x and 0.39 - 0.57 for y. It was noted that the colour
3 coordinates corresponded to a slightly yellow tint due to a low relative luminosity from the
4 blue sub-pixels. This can be corrected by slightly reducing the thickness of the phosphor used
5 for the red and green sub-pixels and increasing the thickness of the Threshold Adjustment
6 Layer described above, all in accordance with the present invention.

7 **Example 4 - Varying Thickness of Phosphor Deposits to Adjust Threshold Voltage**

8 In this Example, as in Example 3, there was only one SrS:Ce deposit for the blue sub-
9 pixels, and one $Zn_{1-x}Mg_xS:Mn$ deposit for the red and green sub-pixels. The phosphors were
10 made and doped as set out in Example 3, with the approximate value of x in the $Zn_{1-x}Mg_xS:Mn$
11 phosphor being between about 0.2 and 0.3. However, in this example, no threshold voltage
12 adjustment layer was used. Rather, the $Zn_{1-x}Mg_xS:Mn$ layer was deposited thick enough to
13 balance the threshold voltages. If nothing else was changed, this would lead to a colour
14 imbalance, with the red and green sub-pixels being more than 3 and 6 times as luminous
15 respectively, as the blue sub-pixels. As a result, the filtered white would be too yellow. In this
16 example, this colour imbalance was solved by making the blue sub-pixels wider than the red or
17 green sub-pixels.

18 The substrates used for this example were 5.1 x 5.1 cm (2 x 2 inch)substrates, as set
19 forth in Example 2.

20 **4.1. Thick Film Substrate**

21 The thick film substrate layers of Example 2 were used to provide the rear substrate,
22 rear row electrode and thick film dielectric layers.

23 **4.2. Diffusion Barrier Layer**

24 The barrier layer consisted of 500 Å of alumina, deposited as in Example 2. No
25 injection layer was used in this example.

26 **4.3. SrS:Ce Layer**

27 A 1.2 - 1.6 μm thick layer of SrS:Ce was deposited by e-beam evaporation, the
28 phosphor being prepared and deposited as described in Example 3.

29 **4.4. SrS:Ce Patterning**

30 The SrS:Ce layer was removed from the red and green sub-pixels using the procedure
31 described in Example 3. The remaining SrS:Ce stripes were about 320 μm wide, with a
32 spacing between the stripes of 220 μm .

1 **4.5. Barrier Layer**

2 A 500 Å layer of undoped ZnS was deposited at this stage by e-beam evaporation. The
3 purpose of this layer was to provide a barrier layer. When this step was omitted, the lower
4 thick film dielectric layer tended to darken during the later annealing step. This layer of
5 undoped ZnS prevented this darkening. It also provided a cleaner interface for the ZnS:Mn,
6 removing the phosphor from any residue that resulted from the SrS:Ce patterning step.

7 **4.6. Zinc Sulfide/ Zinc Magnesium Sulfide Phosphor Layers**

8 A 800 - 1000 Å layer of ZnS:Mn was deposited next, followed by a 4000 - 6000 Å
9 layer of $Zn_{1-x}Mg_xS:Mn$, and then by a 800 - 1000 Å layer of ZnS:Mn. The ZnS:Mn was
10 deposited as described in Example 2, whereas the $Zn_{1-x}Mg_xS:Mn$ was deposited as in Example
11 3.

12 **4.7. Barrier Layer**

13 Another 500 Å barrier layer of ZnS was deposited at this point by e-beam evaporation.

14 **4.8. Zinc Magnesium Sulfide Lift-Off**

15 The resist covering the SrS:Ce on the blue sub-pixels was dissolved in the same way as
16 in Example 3. The rinsing procedure was different in that the substrates were soaked in clean,
17 anhydrous methanol for 2 min. and then dried under a nitrogen flow.

18 **4.9. Barrier Layer**

19 An upper barrier layer of 500 Å of alumina was deposited.

20 **4.10. Phosphor Annealing**

21 The phosphor was annealed at this stage in a belt furnace in air for 10 min. at a peak
22 temperature of 550°C.

23 **4.11. Transparent Electrode Fabrication**

24 The indium tin oxide layer was deposited by sputtering using a current of 2 Amps, a
25 temperature of 25°C, a pressure of 1.06 Pa (8 mTorr), an oxygen flow of 0.2 sccm, and an
26 argon flow of about 70 sccm (balanced to give above pressure), to a thickness of 5000 Å.

27 **4.12. Metal Contact Deposition**

28 The metal contacts were printed using polymer thick film silver paste as in Example 2.

29 **4.13. Filter Plate Attachment and Sealing**

30 These steps were performed as described in Example 2. The filter had the following
31 line widths; red - 60 µm, green - 110 µm, blue - 310 µm. The gaps between the lines (where
32 the colours overlapped) were 20 µm wide. The total pixel width was 540 µm.

1 **4.14. Test Results**

2 Several 5.1 x 5.1 cm (2 x 2 inch) panels were made by the above procedure and were
3 tested as in Example 2. The results of the better panels were as follows:

4	Threshold voltage (blue sub-pixels)	130 - 170 V
5	Threshold voltage (red, green sub-pixels)	160 - 200 V
6	Overall threshold voltage used (<5 cd/m ²)	160 - 180 V
7	Luminosity (white, filtered)	165 - 260 cd/m ²
8	White colour coordinates (x)	0.38 - 0.44
9	White colour coordinates (y)	0.40 - 0.45
10	CIE colour coordinates	Red x=0.62, y=0.38 Green x=0.42, y=0.58 Blue x=0.13, y=0.14

13 In this example, the threshold voltages of the red and green sub-pixels were much
14 higher than those of the blue sub-pixels. This can be prevented by reducing the thickness of
15 the Zn_{1-x}Mg_xS:Mn phosphor and increasing the thickness of the SrS:Ce phosphor. As a result
16 of this discrepancy, the blue sub-pixels were too luminous for the red and green sub-pixels at
17 lower voltages. For this reason, a higher threshold voltage was chosen, such that the filtered
18 luminosity at threshold was as high as 5 cd/m². If the phosphor thicknesses were changed to
19 bring the two threshold voltages in line, the colour balance would be better, the luminosity at
20 threshold voltage would be <1 cd/m², and the total luminosity would be higher.

21 **Example 5 - Single Layer Phosphor Structure with SrS:Ce for Green and Blue, Varying
22 Sub-pixel Widths**

23 This example, like the previous two examples, includes only one SrS:Ce deposition
24 and one ZnS:Mn deposition. As in Example 4, the sub-pixel widths was adjusted in order to
25 balance the colour. In addition, however, a Threshold Voltage Adjustment Layer was used to
26 further increase the threshold voltage of the ZnS:Mn layer without increasing its luminosity.
27 Another difference is in the phosphors that have been used for the different colours. SrS:Ce
28 alone was used for both the blue and green sub-pixels, and ZnS:Mn was used for the red sub-
29 pixels, rather than Zn_{1-x}Mg_xS:Mn, since no green was required from this phosphor.

30 The substrates used were 5.1 x 5.1 cm (2 x 2 inch) substrates, as in Example 2.

31 **5.1. Thick Film Substrate**

32 The thick film substrate layers of Example 2 were used to provide the rear substrate,

1 rear row electrode and thick film dielectric layers.

2 **5.2. Diffusion Barrier Layer**

3 A barrier layer of 500 Å alumina was deposited.

4 **5.3. Injection Layer**

5 An injection layer of 100 Å hafnia was deposited.

6 **5.4. SrS:Ce Phosphor Layer**

7 A 1.2 - 1.4 µm layer of SrS:Ce was deposited by e-beam evaporation as described in

8 Example 4.

9 **5.5. SrS:Ce Patterning**

10 The SrS:Ce layer was removed from the red sub-pixels using the procedure described
11 in Example 3, with removal times of 1 - 2 min. The width of the resulting SrS:Ce lines was
12 470 µm and the gaps between the lines were 70 µm.

13 **5.6. Barrier Layer.**

14 A 300 Å layer of alumina was deposited at this stage by e-beam evaporation. The
15 purpose of this step was to provide a cleaner interface for the ZnS:Mn, removing the phosphor
16 from any residue that resulted from the SrS:Ce patterning step.

17 **5.7. Zinc Sulfide Phosphor Layer**

18 A 4500 Å layer of ZnS:Mn was deposited as described in Example 2.

19 **5.8. Threshold Voltage Adjustment Layer**

20 A layer of 1800 Å thick alumina was deposited in the same manner as for the barrier
21 layer.

22 **5.9. Zinc Sulfide Lift-off**

23 The resist covering the SrS:Ce on the blue sub-pixels was dissolved in the same
24 manner as in Example 4.

25 **5.10. Injection Layer**

26 An upper injection layer of 100 Å of hafnia was deposited.

27 **5.11. Barrier Layer**

28 An upper barrier layer of 500 Å of alumina was deposited.

29 **5.12. Phosphor Annealing**

30 The phosphor was annealed at this stage in a belt furnace in air for 10 min. at a peak
31 temperature of 550°C.

32 **5.13. Transparent Electrode Fabrication**

1 The indium tin oxide electrodes were deposited by sputtering, using a current of 2
2 Amps, a temperature of 25°C, a pressure of 1.06 Pa (8 mTorr), an oxygen flow of 0.2 sccm,
3 and an argon flow of about 70 sccm (balanced to give above pressure), to a thickness of 5000
4 Å.

5 **5.14. Metal Contact Deposition**

6 The metal contacts were made from chromium, followed by Al, sputtered as follows:
7 Cr: power 15 kW, temp. 150°C, pressure 0.26 Pa (2 mTorr), thickness 600 Å;
8 Al: power 10 kW, temp. 25°C, pressure 0.26 Pa (2 mTorr), thickness 6800 Å.

9 **5.15. Filter Plate Attachment and Sealing**

10 These steps were performed as described in Example 2. The filter had the following
11 line widths: red - 60 µm, green - 270 µm, blue - 150 µm. The gaps between the lines (where
12 the colours overlapped) were 20 µm. The total pixel width was 540 µm. The green sub-pixel
13 was much wider than in Example 4. This was because the SrS:Ce was not nearly as bright,
14 even with the green filter, as Zn_{1-x}Mg_xS:Mn, and so the green sub-pixels were made wider to
15 compensate.

16 **5.16. Test Results**

17 Several 5.1 x 5.1 cm (2 x 2 inch) panels were made by this procedure, and tested as in
18 Example 2. The results were as follows:

19	Threshold voltage (blue, green sub-pixels)	140 - 170 V
20	Threshold voltage (red sub-pixels)	130 - 150 V
21	Overall threshold voltage used (<1 cd/m ²)	130 -150 V
22	Luminosity (white, filtered)	40 - 64 cd/m ²
23	White colour coordinates (x)	0.35 - 0.46
24	White colour coordinates (y)	0.39 - 0.42

25 It will be noted that these panels also had good colour saturations, like Example 4. For
26 blue, x~0.13, y~0.15, for green, x~0.23, y~0.58, and for red, x~0.65, y~0.35.

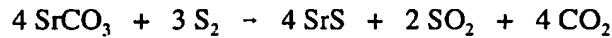
27 **f) Strontium Sulfide Synthesis**

28 The performance of the phosphor structure described above was found to be highly
29 dependent upon the quality of the SrS powder used as a source material for the SrS phosphor.
30 The following preparation was used to maximize luminance efficiency and blue purity.

31 The desired properties of phosphor films comprising 0.12% Ce doped SrS are a
32 luminosity of 80 candelas per square meter or higher, up to 200 cd/m², and colour coordinates

1 of $0.19 < x < 0.20$ and $0.34 < y < 0.40$ corresponding to blue when excited with 80 microsecond
2 pulses having an amplitude of 40 volts above the threshold voltage and a repetition rate of 120
3 pulses/sec. If the preparation procedure for the SrS is not carefully controlled, the luminosity
4 decreases and the colour coordinates shift to x up to 0.3 and y up to 0.5, significantly toward
5 green.

6 In accordance with this invention, the SrS synthesis reaction should be controlled in
7 order to occur homogeneously. Generally, this entails providing a strontium carbonate
8 precursor powder in a dispersed form so that it is substantially uniformly exposed to the
9 process conditions. This can be achieved by using small batches, using volatile, non-
10 contaminating, clean evaporating compounds or solvents which decompose into gaseous
11 products prior to the onset of the reaction, or by using a fluidized bed or tumbler reactor. It is
12 also important to achieve a slow and uniform conversion of a strontium carbonate precursor
13 powder to strontium sulfide, in the presence of sulfur vapours, at an elevated temperature in
14 the range of 800 - 1200 °C. Without such control, variation is observed in the
15 photoluminescent emission spectrum and luminosity of the SrS powder, using broadband
16 ultraviolet illumination, and in the electroluminescent emission spectrum and luminosity
17 efficiency of the deposited SrS phosphor layers made from the powder. The basic synthesis
18 reaction can be written as:



20 The reaction occurs in two steps, with the first step involving the decomposition of the
21 strontium carbonate to oxygen-containing strontium compounds and carbon dioxide, and the
22 second step involving a reaction with sulfur to produce strontium sulfide and sulfur dioxide (or
23 perhaps other sulfur oxides). The interrelationship between these two steps is found to have a
24 significant bearing on the quality of powder that is produced.

25 The reactor for the synthesis consists of a quartz or ceramic tube positioned in the hot
26 zone of a tube furnace into which a strontium carbonate powder is placed. The tube material
27 of the reactor should not react chemically with the reactants or reaction products. In this
28 example, a 3.8 cm (1.5 inch) diameter alumina tube having a length in the hot zone of about 30
29 cm (12 inches) was used. The tube was loaded with about 75 grams of a strontium carbonate
30 powder in the hot zone. The strontium carbonate had a purity level of greater than 99.9% on a
31 metal basis. Powders of such purity may be commercially obtained or generated by
32 precipitating strontium nitrate or strontium hydroxide with ammonium carbonate. The tube

1 was heated gradually, at a rate not exceeding 5 to 10°C/min, to a maximum temperature in the
2 range of 800 to 1200°C. The preferred maximum temperature is about 1100°C.

3 At about the time the maximum temperature is reached, a continuous flow of sulfur
4 vapour is introduced into an argon gas stream (i.e., in an inert atmosphere) at atmospheric
5 pressure entering the reaction tube. The sulfur vapour may be generated by either placing a
6 container containing elemental sulfur at the entrance end of heated reaction tube, or by heating
7 a separate stainless steel container filled with sulfur to between 360 and 440°C which is
8 connected to the entrance end of the reaction tube. An appropriate amount of sulfur vapour is
9 introduced by adjusting the pot temperature and the argon flow rate. A Ferran Scientific mass
10 spectrometer is connected to the exit end of the reaction tube, and the relative concentrations
11 of carbon dioxide and sulfur dioxide are measured. The reaction is terminated when the mass
12 spectrometer reading of a predetermined concentration of sulfur dioxide is reached. This is
13 done by switching off the sulfur flow into the tube and by cooling down the furnace. The
14 sulfur vapour flow is stopped by turning off the sulfur pot heater. The argon flow continues
15 until the furnace is cool enough for unloading the product, typically below 200°C. The firing
16 time at the maximum temperature is typically in the range of 2 to 8 hours, depending on the
17 maximum temperature, the sulfur vapour delivery rate, the strontium carbonate powder
18 packing density and the end point, at which time the reaction is terminated.

19 The end point is considered reached when the mass spectrometer reading of SO₂ falls
20 into the range between 0.001 - 0.01 Pa (1 X 10⁻⁵ to 1 X 10⁻⁴ Torr) in a base pressure of 0.2 - 0.3
21 Pa (2 X 10⁻³ to 3 X 10⁻³ Torr). This results in a small residual quantity of oxygen-containing
22 strontium compounds, or possibly a fraction of that in the form of strontium carbonate, (i.e.,
23 oxygen-containing strontium compounds) remaining in the strontium sulfide product, the
24 presence of which correlates with improved phosphor performance. The most luminous
25 phosphor films have been made using strontium sulfide powders containing about 5 atomic
26 percent of oxygen-containing strontium compounds, but good phosphors may be made over a
27 range of oxide concentrations. The preferred range of concentrations of oxygen-containing
28 strontium compounds is 1 to 10 atomic percent. The correlation between oxide content and
29 phosphor performance is fairly weak, due to the influence of other variables during phosphor
30 preparation. However, it is generally observed that strontium sulfide with too little oxide
31 correlates with a shift from blue to green in photoluminescence from the powder and a
32 deleterious shift from blue to green in electroluminescence of phosphor films prepared

1 therefrom.

2 The strontium carbonate starting powder can be doped with cerium carbonate, cerium
3 fluoride, or another form of cerium additive, or the dopant can be added later as cerium
4 fluoride or cerium sulfide to the resulting strontium sulfide powder, or the dopant may be
5 added prior to phosphor film deposition. No significant dependence of phosphor performance
6 on the method of cerium introduction has been found to exist. The amount of the dopant is
7 preferably in the range of 0.01 to 0.35 mole %, more preferably 0.05 to 0.25%.

8 The initial form of the strontium carbonate powder does have a significant impact on
9 phosphor performance. It is desirable that the powder has a high porosity, and does not fuse
10 during reaction with sulfur. A densely packed strontium carbonate powder specimen or one
11 that fuses during reaction tends to result in green shift in the photoluminescence and
12 electroluminescence of the films deposited with the strontium sulfide powder therefrom, and is
13 thus undesired. A loosely packed powder usually gives the best performance for the phosphor.

14 The impact of the porosity or the dispersed form of the bulk strontium carbonate
15 powder on the quality of the strontium sulfide phosphor is also reflected in the reaction
16 mechanism as evidenced by the relative conversion rate to strontium sulfide at the second
17 stage of the reaction. For a densely packed powder with low porosity, the conversion is
18 usually fast with the onset of sulfur dioxide evolution occurring at about 10 minutes after the
19 onset of carbon dioxide evolution. For a loosely packed powder with high porosity, the onset
20 of sulfur dioxide evolution occurs at a much later time, as long as 100 minutes after the onset
21 of carbon dioxide evolution.

22 The porosity of the powder helps ensure that the process environment is essentially
23 uniform throughout the material being processed, allowing unrestricted diffusion of the sulfur
24 vapour and gaseous reaction products. This is believed to help ensure that the product
25 particles are homogeneous on an atomic scale. Types of atomic scale inhomogeneity include
26 lattice substitutions, interstitial atoms, vacancies and clusters thereof. Lattice substitutions do
27 not necessarily imply that an impurity atom is present, and may include positioning of a
28 strontium atom where a sulfur atom should be, and vice versa. Even though the powder is
29 vaporized during phosphor deposition, clusters of atoms rather than individual atoms may
30 vaporize, preserving atomic scale defects initially present in the source powder used for the
31 deposited films.

32 Several methods to achieve high strontium carbonate powder dispersion or porosity

1 have been developed. One is to mix the strontium carbonate powder with a volatile, clean
2 evaporating non-contaminating powdered compound that decomposes into gaseous products
3 prior to the onset of reactions involving strontium carbonate. Examples of such compounds
4 are high purity powder such as ammonium carbonate, ammonium sulphate and elemental
5 sulfur. The additive can be added giving a weight ratio of additive to strontium carbonate in
6 the range of 1:9 to 1:1, but preferably is in the range of 1:4 to 1:2.5. This method works well
7 with the free flowing strontium carbonate powder made from strontium nitrate and ammonium
8 carbonate.

9 A second method to effect powder porosity or dispersion is to soak the powder in a
10 solvent that penetrates the powder, modifying the surface properties of the strontium carbonate
11 particles to prevent it from fusing during the reaction with sulfur vapour at high temperatures.
12 The strontium carbonate is mixed with a non-contaminating solvent to form a slurry, which is
13 then partially dried in air at ambient temperature or with mild heating depending on the nature
14 of the solvent to form a free flowing powder. The powder should undergo a weight gain of
15 between 5 and 30% as compared to completely dry powder. The partially dried powder can be
16 loaded in the reactor tube according to the usual procedure. The solvent can include, but is not
17 limited to, acetone, methanol, ethanol and water. This method works well with the granular
18 and sticky strontium carbonate powder such as that made from strontium hydroxide and
19 ammonium carbonate.

20 The use of argon as an inert carrier gas is preferred. When forming gas (5% hydrogen
21 in argon) is used in place of argon, green shift in the photoluminescence and
22 electroluminescence of the films deposited from the powder is again observed.

23 Sample size is another significant factor that affects the quality of the strontium sulfide.
24 Large samples of 150 grams of strontium carbonate, also lead to a green shift of emission
25 spectrum of the film. This is believed to be a direct result of the inhomogeneous reaction of
26 the powder with the reactant since repeated regrinding and firing tends to improve the quality
27 of the strontium sulfide.

28 All publications mentioned in this specification are indicative of the level of skill of
29 those skilled in the art to which this invention pertains. All publications are herein
30 incorporated by reference to the same extent as if each individual publication was specifically
31 and individually indicated to be incorporated by reference.

32 The terms and expressions used in this specification are used as terms of description

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1 and not of limitation. There is no intention, in using such terms and expressions, of excluding
2 equivalents of the features shown and described.

1 We claim:

2 1. A patterned phosphor structure having red, green and blue sub-pixel phosphor elements
3 for an AC electroluminescent display, comprising:

4 at least a first and a second phosphor, each emitting light in different ranges of the
5 visible spectrum, but whose combined emission spectra contains red, green and blue light;

6 said at least first and second phosphors being in a layer, arranged in adjacent, repeating
7 relationship to each other to provide a plurality of repeating at least first and second phosphor
8 deposits; and

9 one or more means associated with one or more of the at least first and second
10 phosphor deposits, and which together with the at least first and second phosphor deposits,
11 form the red, green and blue sub-pixel phosphor elements, for setting and equalizing the
12 threshold voltages of the red, green and blue sub-pixel phosphor elements, and for setting the
13 relative luminosities of the red, green and blue sub-pixel phosphor elements so that they bear
14 set ratios to one another at each operating modulation voltage used to generate the desired
15 luminosities for red, green and blue.

16 2. The phosphor structure as set forth in claim 1, wherein the at least first and second
17 phosphor deposits are formed from phosphors of different host materials.

18 3. The phosphor structure as set forth in claim 2, wherein the set luminosity ratios remain
19 substantially constant over the range of operating modulation voltages.

20 4. The phosphor structure as set forth in claim 3, wherein the set luminosity ratios
21 between the red, green and blue sub-pixel phosphor elements is about 3:6:1.

22 5. The phosphor structure as set forth in claim 2, 3 or 4, wherein the means for setting and
23 equalizing the threshold voltages, and for setting the relative luminosities, comprises a
24 threshold voltage adjustment layer of a dielectric material or a semiconductor material located
25 in one or more of the positions of over, under and embedded within one or more of the at least
26 first and second phosphor deposits.

27 6. The phosphor structure as set forth in claim 2, 3, 4 or 5, wherein the means for setting
28 and equalizing the threshold voltages, and for setting the relative luminosities, comprises the at
29 least first and second phosphor deposits being formed with different thicknesses.

30 7. The phosphor structure as set forth in claim 5 or 6, wherein, the means for setting and
31 equalizing the threshold voltages, and for setting the relative luminosities, further comprises
32 varying one or both of the following:

- 1 i. the areas of the phosphor deposits; and
 - 2 ii. the concentrations of a dopant or co-dopant in the phosphor deposits.
- 3 8. The phosphor structure as set forth in claim 7, wherein the at least first and second
4 phosphor deposits are formed from a zinc sulfide phosphor and a strontium sulfide phosphor.
- 5 9. The phosphor structure as set forth in claim 8, wherein the blue sub-pixel elements,
6 and optionally the green sub-pixel elements are formed with a strontium sulfide phosphor, and
7 wherein the red sub-pixel elements, and optionally the green sub-pixel elements are formed
8 from one or more zinc sulfide phosphors.
- 9 10. The phosphor structure as set forth in claim 9, wherein the strontium sulfide phosphor
10 is SrS:Ce and wherein the zinc sulfide phosphor is one or both of ZnS:Mn or $Zn_{1-x}Mg_xS:Mn$,
11 with x being between 0.1 and 0.3.
- 12 11. The phosphor structure as set forth in claim 8, wherein the first phosphor is SrS:Ce and
13 the second phosphor is one or more of ZnS:Mn or $Zn_{1-x}Mg_xS:Mn$, with x being between 0.1
14 and 0.3, and wherein the means for setting and equalizing the threshold voltages and for
15 setting the relative luminosities comprises a further layer of SrS:Ce over the first and second
16 phosphor deposits, whereby the blue sub-pixel elements are provided by SrS:Ce and the red
17 and green sub-pixel elements are provided by SrS:Ce and one or both of ZnS:Mn or $Zn_{1-x}Mg_xS:Mn$.
- 18 12. The phosphor structure as set forth in claim 10, wherein the means for setting and
19 equalizing the threshold voltages and for setting the relative luminosities comprises a
20 threshold voltage adjustment layer over the red and green sub-pixel phosphor deposits.
- 21 13. The phosphor structure as set forth in claim 10, 11 or 12, wherein the means for setting
22 and equalizing the threshold voltages and for setting the relative luminosities comprises the
23 phosphor deposits being formed with different thicknesses.
- 24 14. The phosphor structure as set forth in claim 10, 11, 12 or 13, wherein the means for
25 setting and equalizing the threshold voltages and for setting the relative luminosities comprises
26 varying the areas of one or more of the sub-pixel phosphor deposits.
- 27 15. The phosphor structure as set forth in claim 1, 2, or 14, wherein the means for setting and
28 equalizing the threshold voltages, and for setting the relative luminosities, comprises a
29 threshold voltage adjustment layer selected from the group consisting of one or more of a
30 dielectric material or a semiconductor material, which, at its deposited thickness, does not
31 conduct until the voltage across the patterned phosphor structure exceeds the threshold voltage

1 which the patterned phosphor structure would have without the threshold voltage adjustment
2 layer.

3 16. The phosphor structure as set forth in claim 15, wherein the threshold voltage
4 adjustment layer is selected from the group consisting of binary metal oxides, binary metal
5 sulfides, silica and silicon oxynitride.

6 17. The phosphor structure as set forth in claim 15, wherein the threshold voltage
7 adjustment layer is selected from the group consisting of alumina, tantalum oxide, zinc sulfide,
8 strontium sulfide, silica and silicon oxynitride.

9 18. The phosphor structure as set forth in claim 15, wherein the threshold voltage
10 adjustment layer is selected from the group consisting of alumina and zinc sulfide.

11 19. The phosphor structure as set forth in claim 15, wherein threshold voltage adjustment
12 layer is matched with the at least first or second phosphor deposits, such that if the phosphor
13 deposit is formed from a zinc sulfide phosphor, the threshold voltage adjustment layer, if
14 needed with that phosphor deposit, is a binary metal oxide.

15 20. The phosphor structure as set forth in claim 19, wherein the binary metal oxide is
16 alumina when the phosphor deposit is one or more of ZnS:Mn or Zn_{1-x}Mg_xS:Mn, with x being
17 between 0.1 and 0.3.

18 21. The phosphor structure as set forth in claim 5, 6 or 7, wherein the means for setting and
19 equalizing the threshold voltages and for setting the relative luminosities comprises an
20 additional phosphor layer deposited in one or more of the positions of over, under and
21 embedded within the at least first and second phosphor deposits, having a same or different
22 composition from the at least first and second phosphor deposits.

23 22. The phosphor structure as set forth in claim 5, 6 or 7, wherein the first and second
24 phosphor deposits are a strontium sulfide phosphor providing the blue sub-pixel elements and
25 a zinc sulfide phosphor providing the red and green sub-pixel elements, and wherein the
26 means for setting and equalizing the threshold voltages and for setting the relative luminosities
27 is a threshold voltage adjustment layer selected from the group consisting of one or more of a
28 dielectric material or a semiconductor material in one or more of the positions of over, under
29 and embedded within the zinc sulfide phosphor deposits.

30 23. The phosphor structure as set forth in claim 22, wherein the phosphors are SrS:Ce,
31 which may be codoped with phosphorus, and Zn_{1-x}Mg_xS:Mn, with x being between 0.1 and
32 0.3, and wherein the threshold voltage adjustment layer is a layer of alumina located over the

1 Zn_{1-x}Mg_xS:Mn phosphor deposits.

2 24. The phosphor structure as set forth in claim 5, 6 or 7, wherein the first and second
3 phosphor deposits are a strontium sulfide phosphor providing the blue sub-pixel elements and
4 one or more layers of a zinc sulfide phosphor providing the red and green sub-pixel elements,
5 and wherein the means for setting and equalizing the threshold voltages and for setting the
6 relative luminosities is the strontium sulfide phosphor deposits being formed thicker and wider
7 than the zinc sulfide phosphor deposits.

8 25. The phosphor structure as set forth in claim 24, wherein the phosphors are SrS:Ce for
9 the blue sub-pixel elements, which may be codoped with phosphorus, and for the red and
10 green sub-pixels, Zn_{1-x}Mg_xS:Mn between layers of ZnS:Mn, with x being between 0.1 and 0.3.

11 26. The phosphor structure as set forth in claim 5, 6 or 7, wherein the first and second
12 phosphor deposits are a strontium sulfide phosphor providing the blue and green sub-pixel
13 elements and a zinc sulfide phosphor providing the red sub-pixel elements, and wherein the
14 means for setting and equalizing the threshold voltages and for setting the relative luminosities
15 is a threshold voltage adjustment layer selected from the group consisting of one or more of a
16 dielectric material or a semiconductor material in one or more of the position of over, under
17 and embedded within the zinc sulfide phosphor deposits.

18 27. The phosphor structure as set forth in claim 26, wherein the phosphors are SrS:Ce,
19 which may be codoped with phosphorus, and ZnS:Mn, and wherein the threshold voltage
20 adjustment layer is a layer of alumina located over the ZnS:Mn phosphor deposits.

21 28. An EL laminate for use in an AC electroluminescent display, comprising:
22 a rigid rear substrate;
23 a patterned phosphor structure comprising:
24 at least a first and a second phosphor, each emitting light in different ranges of
25 the visible spectrum, but whose combined emission spectra contains red, green
26 and blue light;
27 said at least first and second phosphors being in a layer, arranged in adjacent,
28 repeating relationship to each other to provide a plurality of repeating at least
29 first and second phosphor deposits; and
30 one or more means associated with one or more of the at least first and second
31 phosphor deposits, and which together with the at least first and second
32 phosphor deposits, form the red, green and blue sub-pixel phosphor elements,

1 for setting and equalizing the threshold voltages of the red, green and blue sub-
2 pixel phosphor elements, and for setting the relative luminosities of the red,
3 green and blue sub-pixel phosphor elements so that they bear set ratios to one
4 another at each operating modulation voltage used to generate the desired
5 luminosities for red, green and blue;

6 front and rear column and row electrodes on either side of the phosphor structure, the
7 rows or columns of the front or rear electrode being aligned with the phosphor sub-pixel
8 elements;

9 a thick film dielectric layer below the patterned phosphor structure formed from a
10 sintered ceramic material having a dielectric constant greater than 500, and having a thickness
11 greater than about 10 μm ; and

12 optionally, optical colour filter means aligned with the red, green and blue phosphor
13 sub-pixel elements for transmitting red, green and blue light emitted from the phosphor sub-
14 pixel elements.

15 29. The EL laminate as set forth in claim 28, wherein the at least first and second phosphor
16 deposits are formed from phosphors of different host materials.

17 30. The EL laminate as set forth in claim 29, wherein the set luminosity ratios remain
18 substantially constant over the range of operating modulation voltages.

19 31. The EL laminate as set forth in claim 30, wherein the set luminosities ratios between
20 the red, green and blue sub-pixel phosphor elements is about 3:6:1.

21 32. The EL laminate as set forth in claim 29, 30 or 31, wherein the means for setting and
22 equalizing the threshold voltages, and for setting the relative luminosities, comprises a
23 threshold voltage adjustment layer of a dielectric material or a semiconductor material located
24 in one or more of the positions of over, under and embedded within one or more of the at least
25 first and second phosphor deposits.

26 33. The EL laminate as set forth in claim 29, 30, 31, or 32, wherein the means for setting
27 and equalizing the threshold voltages, and for setting the relative luminosities, comprises the at
28 least first and second phosphor deposits being formed with different thicknesses.

29 34. The EL laminate as set forth in claim 32 or 33, wherein, the means for setting and
30 equalizing the threshold voltages, and for setting the relative luminosities, further comprises
31 varying one or both of the following:

32 i. the areas of the phosphor deposits; and

- 1 ii. the concentrations of a dopant or co-dopant in the phosphor deposits.
- 2 35. The EL laminate as set forth in claim 34, wherein the at least first and second phosphor
3 deposits are formed from a zinc sulfide phosphor and a strontium sulfide phosphor.
- 4 36. The EL laminate as set forth in claim 35, wherein the blue sub-pixel elements, and
5 optionally the green sub-pixel elements are formed with a strontium sulfide phosphor, and
6 wherein the red sub-pixel elements, and optionally the green sub-pixel elements are formed
7 from one or more zinc sulfide phosphors.
- 8 37. The EL laminate as set forth in claim 36, wherein the strontium sulfide phosphor is
9 SrS:Ce and wherein the zinc sulfide phosphor is one or more of ZnS:Mn or Zn_{1-x}Mg_xS:Mn,
10 with x being between 0.1 and 0.3.
- 11 38. The EL laminate as set forth in claim 35, wherein the first phosphor is SrS:Ce and the
12 second phosphor is one or more of ZnS:Mn or Zn_{1-x}Mg_xS:Mn, with x being between 0.1 and
13 0.3, and wherein the means for setting and equalizing the threshold voltages and for setting the
14 relative luminosities comprises a further layer of SrS:Ce over the first and second phosphor
15 deposits, whereby the blue sub-pixel elements are provided by SrS:Ce and the red and green
16 sub-pixel elements are provided by SrS:Ce and one or both of ZnS:Mn or Zn_{1-x}Mg_xS:Mn.
- 17 39. The EL laminate as set forth in claim 37, wherein the means for setting and equalizing
18 the threshold voltages and for setting the relative luminosities comprises a threshold voltage
19 adjustment layer over the red and green sub-pixel phosphor deposits.
- 20 40. The EL laminate as set forth in claim 37, 38, or 39, wherein the means for setting and
21 equalizing the threshold voltages and for setting the relative luminosities comprises the
22 phosphor deposits being formed with different thicknesses.
- 23 41. The EL laminate as set forth in claim 37, 38, 39 or 40, wherein the means for setting
24 and equalizing the threshold voltages and for setting the relative luminosities comprises
25 varying the areas of one or more of the sub-pixel phosphor deposits.
- 26 42. The EL laminate as set forth claim 28, 29, or 41, wherein the means for setting and
27 equalizing the threshold voltages, and for setting the relative luminosities, comprises a
28 threshold voltage adjustment layer selected from the group consisting of one or more of a
29 dielectric material or a semiconductor material, which, at its deposited thickness, does not
30 conduct until the voltage across the patterned phosphor structure exceeds the threshold voltage
31 which the patterned phosphor structure would have without the threshold voltage adjustment
32 layer.

- 1 43. The EL laminate as set forth in claim 42, wherein the threshold voltage adjustment
2 layer is selected from the group consisting of binary metal oxides, binary metal sulfides, silica
3 and silicon oxynitride.
- 4 44. The EL laminate as set forth in claim 42, wherein the threshold voltage adjustment
5 layer is selected from the group consisting of alumina, tantalum oxide, zinc sulfide, strontium
6 sulfide, silica and silicon oxynitride.
- 7 45. The EL laminate as set forth in claim 42, wherein the threshold voltage adjustment
8 layer is selected from the group consisting of alumina and zinc sulfide.
- 9 46. The EL laminate as set forth in claim 42, wherein threshold voltage adjustment layer is
10 matched with the at least first or second phosphor deposits, such that if the phosphor deposit is
11 formed from a zinc sulfide phosphor, the threshold voltage adjustment layer, if needed with
12 that phosphor deposit, is a binary metal oxide.
- 13 47. The EL laminate as set forth in claim 46, wherein the binary metal oxide is alumina
14 when the phosphor deposit is one or more of ZnS:Mn or Zn_{1-x}Mg_xS:Mn, with x being between
15 0.1 and 0.3.
- 16 48. The EL laminate as set forth in claim 32, 33 or 34, wherein the means for setting and
17 equalizing the threshold voltages and for setting the relative luminosities comprises an
18 additional phosphor layer deposited in one or more of the positions of over, under and
19 embedded within the at least first and second phosphor deposits, having a same or different
20 composition from the at least first and second phosphor deposits.
- 21 49. The EL laminate as set forth in claim 32, 33 or 34, wherein the first and second
22 phosphor deposits are a strontium sulfide phosphor providing the blue sub-pixel elements and
23 a zinc sulfide phosphor providing the red and green sub-pixel elements, and wherein the
24 means for setting and equalizing the threshold voltages and for setting the relative luminosities
25 is a threshold voltage adjustment layer selected from the group consisting of one or more of a
26 dielectric material or a semiconductor material in one or more of the positions of over, under
27 and embedded within the zinc sulfide phosphor deposits.
- 28 50. The EL laminate as set forth in claim 49, wherein the phosphors are SrS:Ce, which
29 may be codoped with phosphorus, and Zn_{1-x}Mg_xS:Mn, with x being between 0.1 and 0.3, and
30 wherein the threshold voltage adjustment layer is a layer of alumina located over the Zn₁₋
31 _xMg_xS:Mn phosphor deposits.
- 32 51. The EL laminate as set forth in claim 32, 33 or 34, wherein the first and second

1 phosphor deposits are a strontium sulfide phosphor providing the blue sub-pixel elements and
2 one or more layers of a zinc sulfide phosphor providing the red and green sub-pixel elements,
3 and wherein the means for setting and equalizing the threshold voltages and for setting the
4 relative luminosities is the strontium sulfide phosphor deposits being formed thicker and wider
5 than the zinc sulfide phosphor deposits.

6 52. The EL laminate as set forth in claim 51, wherein the phosphors are SrS:Ce for the
7 blue sub-pixel elements, which may be codoped with phosphorus, and for the red and green
8 sub-pixels, $Zn_{1-x}Mg_xS:Mn$ between layers of ZnS:Mn, with x being between 0.1 and 0.3.

9 53. The EL laminate as set forth in claim 32, 33 or 34, wherein the first and second
10 phosphor deposits are a strontium sulfide phosphor providing the blue and green sub-pixel
11 elements and a zinc sulfide phosphor providing the red sub-pixel elements, and wherein the
12 means for setting and equalizing the threshold voltages and for setting the relative luminosities
13 is a threshold voltage adjustment layer selected from the group consisting of one or more of a
14 dielectric material or a semiconductor material in one or more of the position of over, under
15 and embedded within the zinc sulfide phosphor deposits.

16 54. The EL laminate as set forth in claim 53, wherein the phosphors are SrS:Ce, which
17 may be codoped with phosphorus, and ZnS:Mn, and wherein the threshold voltage adjustment
18 layer is a layer of alumina located over the ZnS:Mn phosphor deposits.

19 55. The EL laminate as set forth in claims 28, 29, 32, 33 or 34, wherein the thick film
20 dielectric layer is formed from a pressed, sintered ceramic material having, compared to an
21 unpressed, sintered dielectric layer of the same composition, improved dielectric strength,
22 reduced porosity and uniform luminosity in an EL laminate.

23 56. The EL laminate as set forth in claim 35, 50, 52, or 54, wherein the thick film dielectric
24 layer is formed from a pressed, sintered ceramic material having, compared to an unpressed,
25 sintered dielectric layer of the same composition, improved dielectric strength, reduced
26 porosity and uniform luminosity in an EL laminate.

27 57. The EL laminate as set forth in claim 55 or 56, wherein the dielectric layer has been
28 pressed by cold isostatic pressing to reduce the thickness, after sintering, by about 20 to 50%.

29 58. The EL laminate as set forth in claim 57, wherein the pressed ceramic material has a
30 reduced thickness, after sintering, of 30 to 40%.

31 59. The EL laminate as set forth in claim 58, wherein the pressed ceramic material has a
32 thickness, after sintering, of between 10 and 50 μm .

- 1 60. The EL laminate as set forth in claim 58, wherein the pressed ceramic material has a
2 thickness, after sintering, of between 10 and 20 μm .
- 3 61. The EL laminate as set forth in claim 60, wherein the ceramic material is a ferroelectric
4 ceramic material having a dielectric constant greater than 500.
- 5 62. The EL laminate as set forth in claim 61, wherein the ceramic material has a perovskite
6 crystal structure.
- 7 63. The EL laminate as set forth in claim 62, wherein the ceramic material is selected from
8 the group consisting of one or more of BaTiO₃, PbTiO₃, PMN and PMN-PT.
- 9 64. The EL laminate as set forth in claim 62, wherein the ceramic material is selected from
10 the group consisting of BaTiO₃, PbTiO₃, PMN and PMN-PT.
- 11 65. The EL laminate as set forth in claim 62, wherein the ceramic material is PMN-PT.
- 12 66. The EL laminate as set forth in claim 62, 64, or 65, wherein a second ceramic material
13 is formed on the pressed, sintered dielectric layer to further smooth the surface.
- 14 67. The EL laminate as set forth in claim 59, wherein the second ceramic material is a
15 ferroelectric ceramic material deposited by sol gel techniques followed by heating to convert to
16 a ceramic material.
- 17 68. The EL laminate as set forth in claim 67, wherein the second ceramic material has a
18 dielectric constant of at least 20 and a thickness of at least about 1 μm .
- 19 69. The EL laminate as set forth in claim 68, wherein the second ceramic material has a
20 dielectric constant of at least 100.
- 21 70. The EL laminate as set forth in claim 69, wherein the second ceramic material has a
22 thickness in the range of 1 to 3 μm .
- 23 71. The EL laminate as set forth in claim 70, wherein the second ceramic material is a
24 ferroelectric ceramic material having a perovskite crystal structure.
- 25 72. The EL laminate as set forth in claim 71, wherein the second ceramic material is lead
26 zirconium titanate or lead lanthanum zirconate titanate.
- 27 73. The EL laminate as set forth in claim 72, wherein the substrate and the rear electrode
28 are formed from materials which can withstand temperatures of about 850°C.
- 29 74. The EL laminate as set forth in claim 73, wherein the substrate is an alumina sheet.
- 30 75. The EL laminate as set forth in claim 55, 66 or 72, which further comprises, a diffusion
31 barrier layer above the dielectric layer or above the second ceramic material, which diffusion
32 barrier layer is composed of a metal-containing electrically insulating binary compound that is

1 chemically compatible with any adjacent layers and which is precisely stoichiometric.

2 76. The EL laminate as set forth in claim 75, wherein the diffusion barrier layer is formed
3 from a compound which differs from its precise stoichiometric composition by less than 0.1
4 atomic percent.

5 77. The EL laminate as set forth in claim 76, wherein the diffusion barrier layer is formed
6 from alumina, silica, or zinc sulfide.

7 78. The EL laminate as set forth in claim 76, wherein the diffusion barrier is formed from
8 alumina.

9 79. The EL laminate as set forth in claim 77 or 78, wherein the diffusion barrier has a
10 thickness of 100 to 1000 Å.

11 80. The EL laminate as set forth in claim 55, 66, 72 or 75, which further comprises, an
12 injection layer above the dielectric layer, the second ceramic material or the barrier diffusion
13 barrier, to provide a phosphor interface, composed of a binary, dielectric material which is
14 non-stoichiometric in its composition and having electrons in a range of energy for injection
15 into the phosphor layer.

16 81. The EL laminate as set forth in claim 80, wherein the injection layer is formed from a
17 material which has greater than 0.5% atomic deviation from its stoichiometric composition.

18 82. The EL laminate as set forth in claim 81, wherein the injection layer is formed from
19 hafnia or yttria.

20 83. The EL laminate as set forth in claim 82, wherein the injection layer has a thickness of
21 100 to 1000 Å.

22 84. The EL laminate as set forth in claim 75 or 80, wherein an injection layer of hafnia is
23 included with a phosphor formed from a zinc sulfide phosphor, and wherein a diffusion barrier
24 layer of zinc sulfide is used with a phosphor formed from a strontium sulfide phosphor.

25 85. A method of forming a patterned phosphor structure having red, green and blue sub-
26 pixel elements for an AC electroluminescent display, comprising:

27 selecting at least a first and a second phosphor, each emitting light in different ranges
28 of the visible spectrum, but whose combined emission spectra contains red, green and blue
29 light;

30 depositing and patterning said at least first and second phosphors in a layer to form a
31 plurality of repeating at least first and second phosphor deposits arranged in adjacent,
32 repeating relationship to each other; and

1 providing one or more means associated with one or more of the at least first and
2 second phosphor deposits, and which together with the at least first and second phosphor
3 deposits, form the red, green and blue sub-pixel phosphor elements, for setting and equalizing
4 the threshold voltages of the red, green and blue sub-pixel phosphor elements and for setting
5 the relative luminosities of the red, green and blue sub-pixel elements so that they bear set
6 ratios to one another at each modulation voltage used to generate the desired luminosities for
7 red, green and blue; and

8 optionally annealing the patterned phosphor structure so formed.

9 86. The method as set forth in claim 85, wherein the at least first and second phosphor
10 deposits are formed from phosphors of different host materials.

11 87. The method as set forth in claim 86, wherein the set luminosity ratios remain
12 substantially constant over the range of operating modulation voltages.

13 88. The method as set forth in claim 87, wherein the set luminosities ratios between the
14 red, green and blue sub-pixel phosphor elements are about 3:6:1.

15 89. The method as set forth in claim 86, 87 or 88, wherein the patterning of the at least first
16 and second phosphor is achieved by photolithographic techniques, including the steps of:

17 a) depositing a layer of a first phosphor which is to form at least one of the red, green
18 or blue sub-pixel elements;

19 b) removing the first phosphor in regions which are to define the other of the red, green
20 or blue sub-pixel elements, leaving spaced first phosphor deposits;

21 c) depositing the second phosphor material over the first phosphor deposits and in
22 regions which are to define the other of the red, green and blue sub-pixel elements; and

23 d) removing the second phosphor material from above the first phosphor deposits
24 leaving a plurality of repeating first and second phosphor deposits arranged in adjacent,
25 repeating relationship to each other.

26 90. The method as set forth in claim 89, wherein step b) includes:

27 applying a photo-resist to the first phosphor, exposing the photo-resist through a photo-
28 mask, developing the photo-resist, removing the first phosphor in regions that first phosphor is
29 to define as one or more of the red, green and blue sub-pixel elements;

30 and wherein step d) includes:

31 removing by lift-off, the second phosphor and the resist from above the first phosphor
32 deposits.

91. The method as set forth in claim 90, wherein the photo-resist in step b) is a negative resist that is exposed in the regions that the first phosphor is to define as one or more of the red, green and blue sub-pixel elements.

92. The method as set forth in claim 91, wherein the patterning is achieved with only one photo-mask.

93. The method as set forth in claim 86, 87, 88 or 91, wherein the means for setting and equalizing the threshold voltages, and for setting the relative luminosities, comprises a threshold voltage adjustment layer selected from the group consisting of one or more of a dielectric material or a semiconductor material deposited in one or more of the positions of over, under and embedded within one or more of the at least first and second phosphor deposits.

94. The method as set forth in claim 86, 87, 88, 91 or 93, wherein the means for setting and equalizing the threshold voltages, and for setting the relative luminosities, comprises the at least first and second phosphor deposits being deposited with different thicknesses.

95. The method as set forth in claim 93 or 94, wherein, the means for setting and equalizing the threshold voltages, and for setting the relative luminosities, further comprises varying one or both of the following:

- i. the areas of the phosphor deposits; and
 - ii. the concentrations of a dopant or co-dopant in the phosphor deposits.

96. The method as set forth in claim 95, wherein the at least first and second phosphor deposits include a zinc sulfide phosphor and a strontium sulfide phosphor.

97. The method as set forth in claim 96, wherein the blue sub-pixel elements, and optionally the green sub-pixel elements are formed with a strontium sulfide phosphor, and wherein the red sub-pixel elements, and optionally the green sub-pixel elements are formed from one or more zinc sulfide phosphors.

98. The method as set forth in claim 97, wherein the strontium sulfide phosphor is SrS:Ce and wherein the zinc sulfide phosphor is one or more of ZnS:Mn or Zn_{1-x}Mg_xS:Mn, with x being between 0.1 and 0.3.

99. The method as set forth in claim 96, wherein the first phosphor is SrS:Ce and the second phosphor is one or more of ZnS:Mn or $Zn_{1-x}Mg_xS:Mn$, with x being between 0.1 and 0.3, and wherein the means for setting and equalizing the threshold voltages and for setting the relative luminosities is provided by depositing a further layer of SrS:Ce over the first and

1 second phosphor deposits, whereby the blue sub-pixel elements are provided by SrS:Ce and
2 the red and green sub-pixel elements are provided by SrS:Ce and one or more of ZnS:Mn or
3 $Zn_{1-x}Mg_xS:Mn$.

4 100. The method as set forth in claim 98, wherein the means for setting and equalizing the
5 threshold voltages and for setting the relative luminosities are provided by depositing a
6 threshold voltage adjustment layer over one or more of the red and green sub-pixel phosphor
7 deposits.

8 101. The method as set forth in claim 98, 99 or 100, wherein the means for setting and
9 equalizing the threshold voltages and for setting the relative luminosities is provided by
10 depositing the phosphor, and thus forming the phosphor deposits, with different thicknesses.

11 102. The method as set forth in claim 98, 99, 100 or 101, wherein the means for setting and
12 equalizing the threshold voltages and for setting the relative luminosities is provided by
13 varying the areas of one or more of the sub-pixel phosphor deposits.

14 103. The method as set forth in claim 85, 86 or 102, wherein the means for setting and
15 equalizing the threshold voltages, and for setting the relative luminosities, is provided by
16 depositing over one or more of the red, green and blue sub-pixel deposits, a threshold voltage
17 adjustment layer selected from the group consisting of one or more of a dielectric material or a
18 semiconductor material, which, at its deposited thickness, does not conduct until the voltage
19 across the patterned phosphor structure exceeds the threshold voltage which the patterned
20 phosphor structure would have without the threshold voltage adjustment layer.

21 104. The method as set forth in claim 103, wherein the threshold voltage adjustment layer is
22 selected from the group consisting of binary metal oxides, binary metal sulfides, silica and
23 silicon oxynitride.

24 105. The method as set forth in claim 103, wherein the threshold voltage adjustment layer is
25 selected from the group consisting of alumina, tantalum oxide, zinc sulfide, strontium sulfide,
26 silica and silicon oxynitride.

27 106. The method as set forth in claim 103, wherein the threshold voltage adjustment layer is
28 selected from the group consisting of alumina and zinc sulfide.

29 107. The method as set forth in claim 103, wherein threshold voltage adjustment layer is
30 matched with the at least first or second phosphor deposits, such that if the phosphor deposit is
31 formed from a zinc sulfide phosphor, the threshold voltage adjustment layer, if needed with
32 that phosphor deposit, is a binary metal oxide, and if the phosphor deposit is formed from a

1 strontium sulfide phosphor, the threshold voltage adjustment layer, if needed with that
2 phosphor deposit, is a binary metal sulfide.

3 108. The method as set forth in claim 107, wherein the binary metal oxide is alumina when
4 the phosphor deposit is one or more of $ZnS:Mn$ or $Zn_{1-x}Mg_xS:Mn$, with x being between 0.1
5 and 0.3.

6 109. The method as set forth in claim 93, 94, or 98, wherein the means for setting and
7 equalizing the threshold voltages and for setting the relative luminosities comprises an
8 additional phosphor layer deposited in one or more of the positions of over, under and
9 embedded within the at least first and second phosphor deposits, having a same or different
10 composition from the at least first and second phosphor deposits.

11 110. The method as set forth in claim 93, 94 or 95, wherein the first and second phosphor
12 deposits are a strontium sulfide phosphor providing the blue sub-pixel elements and a zinc
13 sulfide phosphor providing the red and green sub-pixel elements, and wherein the means for
14 setting and equalizing the threshold voltages and for setting the relative luminosities is
15 provided by depositing a threshold voltage adjustment layer selected from the group consisting
16 of one or more of a dielectric material or a semiconductor material in one or more of the
17 positions of over, under and embedded within the zinc sulfide phosphor deposits.

18 111. The method as set forth in claim 110, wherein the phosphors are $SrS:Ce$, which may be
19 codoped with phosphorus, and $Zn_{1-x}Mg_xS:Mn$, with x being between 0.1 and 0.3, and wherein
20 the threshold voltage adjustment layer is a layer of alumina deposited over the $Zn_{1-x}Mg_xS:Mn$
21 phosphor deposits.

22 112. The method as set forth in claim 93, 94 or 95, wherein the first and second phosphor
23 deposits are a strontium sulfide phosphor providing the blue sub-pixel elements and one or
24 more layers of a zinc sulfide phosphor providing the red and green sub-pixel elements, and
25 wherein the means for setting and equalizing the threshold voltages and for setting the relative
26 luminosities is provided by forming the strontium sulfide phosphor deposits thicker and wider
27 than and the zinc sulfide phosphor deposits.

28 113. The method as set forth in claim 112, wherein the phosphors are $SrS:Ce$ for the blue
29 sub-pixel elements, which may be codoped with phosphorus, and for the red and green sub-
30 pixels, $Zn_{1-x}Mg_xS:Mn$ between layers of $ZnS:Mn$, with x being between 0.1 and 0.3.

31 114. The method as set forth in claim 93, 94 or 95, wherein the first and second phosphor
32 deposits are a strontium sulfide phosphor providing the blue and green sub-pixel elements and

1 a zinc sulfide phosphor providing the red sub-pixel elements, and wherein the means for
2 setting and equalizing the threshold voltages and for setting the relative luminosities is
3 provided by depositing a threshold voltage adjustment layer selected from the group consisting
4 of one or more of a dielectric material or a semiconductor material in one or more of the
5 positions of over, under and embedded within the zinc sulfide phosphor deposits.

6 115. The method as set forth in claim 114, wherein the phosphors are SrS:Ce, which may be
7 codoped with phosphorus, and ZnS:Mn, and wherein the threshold voltage adjustment layer is
8 a layer of alumina deposited over the ZnS:Mn phosphor deposits.

9 116. The method as set forth in claims 91, wherein one or both of the first and second
10 phosphors is susceptible to hydrolysis, wherein the negative resist is a polyisoprene-based
11 resist, wherein the first phosphor is removed with an acid etchant solution, and wherein the
12 second phosphor is removed with a non-aqueous, predominately polar, aprotic solvent
13 solution.

14 117. The method as set forth in claim 116, wherein the first and second phosphor deposits
15 are a strontium sulfide phosphor and a zinc sulfide phosphor, and wherein the predominately
16 polar, aprotic solvent solution is toluene, with a minor amount of methanol.

17 118. The method as set forth in claim 117, wherein the first and second phosphor deposits
18 are patterned in a layer from SrS:Ce and ZnS:Mn, and an additional phosphor layer of SrS:Ce
19 is deposited over the patterned layer such that, the SrS:Ce deposits form the blue sub-pixel
20 elements, and the ZnS:Mn deposits overlaid with the SrS:Ce deposits form the red and green
21 sub-pixel elements, the patterning being achieved by:

22 a) depositing a layer of the SrS:Ce which is to form the blue sub-pixel elements;

23 b) applying the negative photoresist on the SrS:Ce, exposing the photoresist in those
24 regions which are to form the blue sub-pixel elements, and removing the SrS:Ce and the
25 unexposed photoresist in those regions which are to define the red and green sub-pixel
26 elements, leaving spaced SrS:Ce deposit;

27 c) depositing the ZnS:Mn to cover both the SrS:Ce deposits and the regions where the
28 SrS:Ce has been removed;

29 d) optionally depositing an injection layer;

30 e) removing by lift-off, the ZnS:Mn, the photoresist and the optional injection layer in
31 the regions above SrS:Ce, to form a plurality of repeating first and second phosphor deposits
32 arranged in adjacent, repeating relationship to each other; and

1 f) providing the means for setting and equalizing the threshold voltages and setting the
2 relative luminosities by depositing an additional layer of SrS:Ce over the first and second
3 phosphor deposits.

4 119. The method as set forth in claim 117, wherein the first and second phosphor deposits
5 are a strontium sulfide phosphor providing the blue sub-pixel elements and a zinc sulfide
6 phosphor providing the red and green sub-pixel elements, and wherein the means for setting
7 and equalizing the threshold voltages is a threshold voltage adjustment layer selected from the
8 group consisting of one or more of a dielectric material or a semiconductor material deposited
9 in one or more of the positions of over, under and embedded within the zinc sulfide phosphor
10 deposits.

11 120. The method as set forth in claim 119, wherein the phosphors are SrS:Ce, which may be
12 codoped with phosphorus, and $Zn_{1-x}Mg_xS:Mn$, with x being between 0.1 and 0.3, wherein the
13 threshold voltage adjustment layer is a layer of alumina deposited over the $Zn_{1-x}Mg_xS:Mn$
14 phosphor, and wherein the patterning is achieved by:

- 15 a) depositing a layer of the SrS:Ce which is to form the blue sub-pixel elements;
- 16 b) applying the negative photoresist on the SrS:Ce, exposing the photoresist in those
17 regions which are to form the blue sub-pixel elements, and removing the SrS:Ce and the
18 unexposed photoresist in those regions which are to define the red and green sub-pixel
19 elements, leaving spaced SrS:Ce deposits;
- 20 c) depositing the $Zn_{1-x}Mg_xS:Mn$ to cover both the SrS:Ce deposits and the regions
21 where the SrS:Ce has been removed;
- 22 d) optionally depositing an injection layer;
- 23 e) depositing the threshold voltage adjustment layer above the $Zn_{1-x}Mg_xS:Mn$; and
- 24 e) removing by lift-off, the $Zn_{1-x}Mg_xS:Mn$, the photoresist, the threshold voltage
25 adjustment layer, and the optional injection layer in the regions above SrS:Ce, to form a
26 plurality of repeating first and second phosphor deposits arranged in adjacent, repeating
27 relationship to each other.

28 121. The method as set forth in claim 117, wherein the first and second phosphor deposits
29 are a strontium sulfide phosphor providing the blue sub-pixel elements and a zinc sulfide
30 phosphor providing the red and green sub-pixel elements, and wherein the means for setting
31 and equalizing the threshold voltages and setting the relative luminosities is provided by
32 forming the strontium sulfide phosphor deposits thicker and with greater area than the zinc

1 sulfide phosphor deposits.

2 122. The method as set forth in claim 121, wherein the phosphors are SrS:Ce, which may be
3 codoped with phosphorus, and Zn_{1-x}Mg_xS:Mn between layers of ZnS:Mn, with x being
4 between 0.1 and 0.3, and wherein the patterning is achieved by:

5 a) depositing a layer of the SrS:Ce which is to form the blue sub-pixel elements;

6 b) applying the negative photoresist on the SrS:Ce, exposing the photoresist in those
7 regions which are to form the blue sub-pixel elements, and removing the SrS:Ce and the
8 unexposed photoresist in those regions which are to define the red and green sub-pixel
9 elements, leaving spaced SrS:Ce deposits;

10 c) depositing the a layer of ZnS:Mn, then a layer of Zn_{1-x}Mg_xS:Mn, and then a layer of
11 ZnS:Mn to cover both the SrS:Ce deposits and the regions where the SrS:Ce has been
12 removed;

13 d) optionally depositing an injection layer;

14 e) removing by lift-off, the ZnS:Mn and the Zn_{1-x}Mg_xS:Mn, the photoresist, and the
15 optional injection layer in the regions above SrS:Ce, to form a plurality of repeating first and
16 second phosphor deposits arranged in adjacent, repeating relationship to each other.

17 123. The method as set forth in claim 117, wherein the first and second phosphor deposits
18 are a strontium sulfide phosphor providing the blue and green sub-pixel elements and a zinc
19 sulfide phosphor providing the red sub-pixel elements, and wherein the means for setting and
20 equalizing the threshold voltages is provided by depositing a threshold voltage adjustment
21 layer selected from the group consisting of one or more of a dielectric material or a
22 semiconductor material in one or more of the positions of over, under and embedded within
23 the zinc sulfide phosphor deposits.

24 124. The method as set forth in claim 123, wherein the phosphors are SrS:Ce, which may be
25 codoped with phosphorus, and ZnS:Mn, wherein the threshold voltage adjustment layer is a
26 layer of alumina located over the ZnS:Mn phosphor, and wherein the patterning is achieved
27 by:

28 a) depositing a layer of the SrS:Ce which is to form the blue and green sub-pixel
29 elements;

30 b) applying the negative photoresist on the SrS:Ce, exposing the photoresist in those
31 regions which are to form the blue and green sub-pixel elements, and removing the SrS:Ce and
32 the unexposed photoresist in those regions which are to define the red sub-pixel elements,

1 leaving spaced SrS:Ce deposits for the blue and green sub-pixel elements which are wider than
2 the regions left for the red sub-pixel elements;
3 c) depositing an optional layer of alumina as a barrier diffusion layer;
4 d) depositing the ZnS:Mn to cover both the SrS:Ce deposits and the regions where the
5 SrS:Ce has been removed;
6 e) depositing the threshold voltage adjustment layer above the Zn:S:Mn; and
7 f) removing by lift-off, the optional barrier diffusion layer, the ZnS:Mn, the
8 photoresist, and the threshold voltage adjustment layer in the regions above SrS:Ce, to form a
9 plurality of repeating first and second phosphor deposits arranged in adjacent, repeating
10 relationship to each other.

11 125. A method of forming a thick film dielectric layer in an EL laminate of the type
12 including one or more phosphor layers sandwiched between a front and a rear electrode, the
13 phosphor layer being separated from the rear electrode by the thick film dielectric layer,
14 comprising:

15 depositing a ceramic material in one or more layers by a thick film technique to form a
16 dielectric layer having a thickness of 10 to 300 μm ;
17 pressing the dielectric layer to form a densified layer with reduced porosity and surface
18 roughness; and

19 sintering the dielectric layer to form a pressed, sintered dielectric layer which, in an EL
20 laminate, has an improved uniform luminosity over an unpressed, sintered dielectric layer of
21 the same composition.

22 126. The method as set forth in claim 125, wherein the dielectric layer is deposited on a
23 rigid substrate providing the rear electrode.

24 127. The method as set forth in claim 125, wherein the pressing is isostatic pressing.

25 128. The method as set forth in claim 126, wherein the pressing is cold isostatic pressing at
26 up to 350,000 kPa to reduce the thickness of the dielectric layer, after sintering, by about 20 to
27 50%.

28 129. The method as set forth in claim 128, wherein the ceramic material is deposited by
29 screen printing, in one or more layers, and is dried prior to pressing.

30 130. The method as set forth in claim 129, wherein the ceramic material is pressed to reduce
31 the thickness, after sintering, by 30 to 40%.

32 131. The method as set forth in claim 130, wherein the ceramic material is pressed to a

- 1 thickness, after sintering, of between 10 and 50 μm .
- 2 132. The method as set forth in claim 130, wherein the ceramic material is pressed to a
3 thickness, after sintering, of between 10 and 20 μm .
- 4 133. The method as set forth in claim 132, wherein the dielectric layer has a deposited
5 thickness of 20 to 50 μm .
- 6 134. The method as set forth in claim 132 or 133, wherein the ceramic material is a
7 ferroelectric ceramic material having a dielectric constant greater than 500.
- 8 135. The method as set forth in claim 134, wherein the ceramic material has a perovskite
9 crystal structure.
- 10 136. The method as set forth in claim 135, wherein the ceramic material is selected from the
11 group consisting of one or more of BaTiO₃, PbTiO₃, PMN and PMN-PT.
- 12 137. The method as set forth in claim 135, wherein the ceramic material is selected from the
13 group consisting of BaTiO₃, PbTiO₃, PMN and PMN-PT.
- 14 138. The method as set forth in claim 137, wherein the ceramic material is PMN-PT.
- 15 139. The method as set forth in claim 136, 137, or 138, wherein a second ceramic material
16 is formed on the pressed, sintered dielectric layer to further smooth the surface.
- 17 140. The method as set forth in claim 139, wherein the second ceramic material is a
18 ferroelectric ceramic material which is deposited by a sol gel technique to form a sol gel layer.
- 19 141. The method as set forth in claim 140, wherein the second ceramic material has a
20 dielectric constant of at least 20 and a thickness of at least about 1 μm .
- 21 142. The method as set forth in claim 141, wherein the second ceramic material has a
22 dielectric constant of at least 100.
- 23 143. The method as set forth in claim 142, wherein the second ceramic material has a
24 thickness in the range of 1 to 3 μm .
- 25 144. The method as set forth in claim 143, wherein the second ceramic material is deposited
26 by a sol gel techniques selected from spin deposition or dipping, followed by heating to
27 convert to a ceramic material.
- 28 145. The method as set forth in claim 144, wherein the second ceramic material is a
29 ferroelectric ceramic material having a perovskite crystal structure.
- 30 146. The method as set forth in claim 145, wherein the second ceramic material is lead
31 zirconium titanate or lead lanthanum zirconate titanate.
- 32 147. The method as set forth in claim 125, 139 or 146, which further comprises, prior to

1 forming the dielectric layer, providing a substrate having sufficient rigidity to support the
2 laminate, and forming the rear electrode on the substrate.

3 148. The method as set forth in claim 147, wherein the substrate and the rear electrode are
4 formed from materials which can withstand temperatures of about 850°C.

5 149. The method as set forth in claim 148, wherein the substrate is an alumina sheet.

6 150. The method as set forth in claim 125, 139 or 149, which further comprises, depositing
7 a diffusion barrier layer above the dielectric layer or above the second ceramic material, which
8 diffusion barrier layer is composed of a metal-containing electrically insulating binary
9 compound that is chemically compatible with any adjacent layers and which is precisely
10 stoichiometric.

11 151. The method as set forth in claim 150, wherein the diffusion barrier layer is formed
12 from a compound which differs from its precise stoichiometric composition by less than 0.1
13 atomic percent.

14 152. The method as set forth in claim 151, wherein the diffusion barrier layer is formed
15 from alumina, silica, or zinc sulfide.

16 153. The method as set forth in claim 152, wherein the diffusion barrier is formed from
17 alumina.

18 154. The method as set forth in claim 153, wherein the diffusion barrier has a thickness of
19 100 to 1000 Å.

20 155. The method as set forth in claim 125, 139 or 150, which further comprises, depositing
21 an injection layer above the dielectric layer, the second ceramic material or the barrier
22 diffusion barrier, to provide a phosphor interface, composed of a binary, dielectric material
23 which is non-stoichiometric in its composition and having electrons in a range of energy for
24 injection into the phosphor layer.

25 156. The method as set forth in claim 155, wherein the injection layer is formed from a
26 material which has greater than 0.5% atomic deviation from its stoichiometric composition.

27 157. The method as set forth in claim 156, wherein the injection layer is formed from hafnia
28 or yttria.

29 158. The method as set forth in claim 157, wherein the injection layer has a thickness of 100
30 to 1000 Å.

31 159. The method as set forth in claim 156 or 158, wherein the injection layer is hafnia when
32 the phosphor is a zinc sulfide phosphor, and wherein a diffusion barrier layer of zinc sulfide is

1 used with a strontium sulfide phosphor.

2 160. A combined substrate and dielectric layer component for use in an EL laminate,
3 comprising:

4 a substrate providing a rear electrode; and

5 a thick film dielectric layer formed on the substrate from a pressed, sintered ceramic
6 material having, compared to an unpressed, sintered dielectric layer of the same composition,
7 improved dielectric strength, reduced porosity and uniform luminosity in an EL laminate.

8 161. The combined substrate and dielectric layer component as set forth in claim 160,
9 formed on a rigid substrate providing a rear electrode.

10 162. The combined substrate and dielectric layer component as set forth in claim 161,
11 wherein the dielectric layer has been pressed by cold isostatic pressing to reduce the thickness,
12 after sintering, by about 20 to 50%.

13 163. The combined substrate and dielectric layer component as set forth in claim 162,
14 wherein the pressed ceramic material has a reduced thickness, after sintering, of 30 to 40%.

15 164. The combined substrate and dielectric layer component as set forth in claim 163,
16 wherein the pressed ceramic material has a thickness, after sintering, of between 10 and 50
17 μm .

18 165. The combined substrate and dielectric layer component as set forth in claim 163,
19 wherein the pressed ceramic material has a thickness, after sintering, of between 10 and 20
20 μm .

21 166. The combined substrate and dielectric layer component as set forth in claim 165,
22 wherein the ceramic material is a ferroelectric ceramic material having a dielectric constant
23 greater than 500.

24 167. The combined substrate and dielectric layer component as set forth in claim 166,
25 wherein the ceramic material has a perovskite crystal structure.

26 168. The combined substrate and dielectric layer component as set forth in claim 167,
27 wherein the ceramic material is selected from the group consisting of one or more of BaTiO_3 ,
28 PbTiO_3 , PMN and PMN-PT.

29 169. The combined substrate and dielectric layer component as set forth in claim 167,
30 wherein the ceramic material is selected from the group consisting of BaTiO_3 , PbTiO_3 , PMN
31 and PMN-PT.

32 170. The combined substrate and dielectric layer component as set forth in claim 167,

1 wherein the ceramic material is PMN-PT.

2 171. The combined substrate and dielectric layer component as set forth in claim 168, 169,
3 or 170, wherein a second ceramic material is formed on the pressed, sintered dielectric layer to
4 further smooth the surface.

5 172. The combined substrate and dielectric layer component as set forth in claim 171,
6 wherein the second ceramic material is a ferroelectric ceramic material deposited by sol gel
7 techniques followed by heating to convert to a ceramic material.

8 173. The combined substrate and dielectric layer component as set forth in claim 172,
9 wherein the second ceramic material has a dielectric constant of at least 20 and a thickness of
10 at least about 1 μm .

11 174. The combined substrate and dielectric layer component as set forth in claim 173,
12 wherein the second ceramic material has a dielectric constant of at least 100.

13 175. The combined substrate and dielectric layer component as set forth in claim 174,
14 wherein the second ceramic material has a thickness in the range of 1 to 3 μm .

15 176. The combined substrate and dielectric layer component as set forth in claim 175,
16 wherein the second ceramic material is a ferroelectric ceramic material having a perovskite
17 crystal structure.

18 177. The combined substrate and dielectric layer component as set forth in claim 176,
19 wherein the second ceramic material is lead zirconium titanate or lead lanthanum zirconate
20 titanate.

21 178. The combined substrate and dielectric layer component as set forth in claim 160, 171,
22 or 177, wherein the combined substrate and dielectric layer component is formed on a rigid
23 substrate, on which is formed the rear electrode.

24 179. The combined substrate and dielectric layer component as set forth in claim 178,
25 wherein the substrate and the rear electrode are formed from materials which can withstand
26 temperatures of about 850°C.

27 180. The combined substrate and dielectric layer component as set forth in claim 179,
28 wherein the substrate is an alumina sheet.

29 181. The combined substrate and dielectric layer component as set forth in claim 160, 171,
30 or 178, which further comprises, a diffusion barrier layer above the dielectric layer or above
31 the second ceramic material, which diffusion barrier layer is composed of a metal-containing
32 electrically insulating binary compound that is chemically compatible with any adjacent layers

1 and which is precisely stoichiometric.

2 182. The combined substrate and dielectric layer component as set forth in claim 181,
3 wherein the diffusion barrier layer is formed from a compound which differs from its precise
4 stoichiometric composition by less than 0.1 atomic percent.

5 183. The combined substrate and dielectric layer component as set forth in claim 182,
6 wherein the diffusion barrier layer is formed from alumina, silica, or zinc sulfide.

7 184. The combined substrate and dielectric layer component as set forth in claim 182,
8 wherein the diffusion barrier is formed from alumina.

9 185. The combined substrate and dielectric layer component as set forth in claim 183 or
10 184, wherein the diffusion barrier has a thickness of 100 to 1000 Å.

11 186. The combined substrate and dielectric layer component as set forth in claim 160, 171,
12 178 or 181, which further comprises, an injection layer above the dielectric layer, the second
13 ceramic material or the barrier diffusion barrier, to provide a phosphor interface, composed of
14 a binary, dielectric material which is non-stoichiometric in its composition and having
15 electrons in a range of energy for injection into the phosphor layer.

16 187. The combined substrate and dielectric layer component as set forth in claim 186,
17 wherein the injection layer is formed from a material which has greater than 0.5% atomic
18 deviation from its stoichiometric composition.

19 188. The combined substrate and dielectric layer component as set forth in claim 187,
20 wherein the injection layer is formed from hafnia or yttria.

21 189. The combined substrate and dielectric layer component as set forth in claim 188,
22 wherein the injection layer has a thickness of 100 to 1000 Å.

23 190. The combined substrate and dielectric layer component as set forth in claim 187 or
24 189, wherein the injection layer is hafnia with a zinc sulfide phosphor, and wherein a diffusion
25 barrier layer of zinc sulfide is used with a strontium sulfide phosphor.

26 191. An EL laminate, comprising:

27 a planar phosphor layer;

28 a front and rear planar electrode on either side of the phosphor layer;

29 a rear substrate providing the rear electrode, the rear substrate having sufficient rigidity
30 to support the laminate; and

31 a thick film dielectric layer on the rigid substrate providing the rear electrode, the thick
32 film dielectric layer being formed from a pressed, sintered ceramic material having, compared

- 1 to an unpressed, sintered dielectric layer of the same composition, improved dielectric
2 strength, reduced porosity and uniform luminosity in an EL laminate.
- 3 192. The EL laminate as set forth in claim 191, formed on a rigid substrate providing a rear
4 electrode.
- 5 193. The EL laminate as set forth in claim 191 or 192, wherein the dielectric layer has been
6 pressed by cold isostatic pressing to reduce the thickness, after sintering, by about 20 to 50%.
- 7 194. The EL laminate as set forth in claim 193, wherein the pressed ceramic material has a
8 reduced thickness, after sintering, of 30 to 40%.
- 9 195. The EL laminate as set forth in claim 194, wherein the pressed ceramic material has a
10 thickness, after sintering, of between 10 and 50 μm .
- 11 196. The EL laminate as set forth in claim 194, wherein the pressed ceramic material has a
12 thickness, after sintering, of between 10 and 20 μm .
- 13 197. The EL laminate as set forth in claim 196, wherein the ceramic material is a
14 ferroelectric ceramic material having a dielectric constant greater than 500.
- 15 198. The EL laminate as set forth in claim 197, wherein the ceramic material has a
16 perovskite crystal structure.
- 17 199. The EL laminate as set forth in claim 198, wherein the ceramic material is selected
18 from the group consisting of one or more of BaTiO₃, PbTiO₃, PMN and PMN-PT.
- 19 200. The EL laminate as set forth in claim 198, wherein the ceramic material is selected
20 from the group consisting of BaTiO₃, PbTiO₃, PMN and PMN-PT.
- 21 201. The EL laminate as set forth in claim 198, wherein the ceramic material is PMN-PT.
- 22 202. The EL laminate as set forth in claim 199, 200 or 201, wherein a second ceramic
23 material is formed on the pressed, sintered dielectric layer to further smooth the surface.
- 24 203. The EL laminate as set forth in claim 202, wherein the second ceramic material is a
25 ferroelectric ceramic material deposited by sol gel techniques followed by heating to convert to
26 a ceramic material.
- 27 204. The EL laminate as set forth in claim 203, wherein the second ceramic material has a
28 dielectric constant of at least 20 and a thickness of at least about 1 μm .
- 29 205. The EL laminate as set forth in claim 204, wherein the second ceramic material has a
30 dielectric constant of at least 100.
- 31 206. The EL laminate as set forth in claim 205, wherein the second ceramic material has a
32 thickness in the range of 1 to 3 μm .

- 1 207. The EL laminate as set forth in claim 206, wherein the second ceramic material is a
2 ferroelectric ceramic material having a perovskite crystal structure.
- 3 208. The EL laminate as set forth in claim 207, wherein the second ceramic material is lead
4 zirconium titanate or lead lanthanum zirconate titanate.
- 5 209. The EL laminate as set forth in claim 191, 202, or 208, wherein the EL laminate is
6 formed on a rigid substrate, on which is formed the rear electrode.
- 7 210. The EL laminate as set forth in claim 209, wherein the substrate and the rear electrode
8 are formed from materials which can withstand temperatures of about 850°C.
- 9 211. The EL laminate as set forth in claim 210, wherein the substrate is an alumina sheet.
- 10 212. The EL laminate as set forth in claim 191, 202, or 209, which further comprises, a
11 diffusion barrier layer above the dielectric layer or above the second ceramic material, which
12 diffusion barrier layer is composed of a metal-containing electrically insulating binary
13 compound that is chemically compatible with any adjacent layers and which is precisely
14 stoichiometric.
- 15 213. The EL laminate as set forth in claim 212, wherein the diffusion barrier layer is formed
16 from a compound which differs from its precise stoichiometric composition by less than 0.1
17 atomic percent.
- 18 214. The EL laminate as set forth in claim 213, wherein the diffusion barrier layer is formed
19 from alumina, silica, or zinc sulfide.
- 20 215. The EL laminate as set forth in claim 213, wherein the diffusion barrier is formed from
21 alumina.
- 22 216. The EL laminate as set forth in claim 214 or 215, wherein the diffusion barrier has a
23 thickness of 100 to 1000 Å.
- 24 217. The EL laminate as set forth in claim 191, 202, 209 or 212, which further comprises,
25 an injection layer above the dielectric layer, the second ceramic material or the barrier
26 diffusion barrier, to provide a phosphor interface, composed of a binary, dielectric material
27 which is non-stoichiometric in its composition and having electrons in a range of energy for
28 injection into the phosphor layer.
- 29 218. The EL laminate as set forth in claim 217, wherein the injection layer is formed from a
30 material which has greater than 0.5% atomic deviation from its stoichiometric composition.
- 31 219. The EL laminate as set forth in claim 218, wherein the injection layer is formed from
32 hafnia or yttria.

- 1 220. The EL laminate as set forth in claim 219, wherein the injection layer has a thickness
2 of 100 to 1000 Å.
- 3 221. The EL laminate as set forth in claim 218 or 220, wherein the injection layer is hafnia
4 with a zinc sulfide phosphor, and wherein a diffusion barrier layer of zinc sulfide is used with
5 a strontium sulfide phosphor.
- 6 222. A method of synthesizing strontium sulfide, comprising:
7 providing a source of high purity strontium carbonate in a dispersed form;
8 heating the strontium carbonate in a reactor with gradual heating up to a maximum
9 temperature in the range of 800 to 1200°C;
10 contacting the heated strontium carbonate with a flow of sulfur vapours formed by
11 heating elemental sulfur in the reactor to at least 300°C in an inert atmosphere; and
12 terminating the reaction by stopping the flow of sulfur at a point when sulfur dioxide or
13 carbon dioxide in the reaction gas reaches an amount which correlates with an amount of
14 oxygen in oxygen-containing strontium compounds in the reaction product which is in the
15 range of 1 to 10 atomic percent.
- 16 223. The method as set forth in claim 222, wherein the sulfur is heated in the temperature
17 range of 360 to 440°C.
- 18 224. The method as set forth in claim 222 or 223, wherein the strontium carbonate is
19 provided in a dispersed form by mixing with one or more volatile, non-contaminating, clean
20 evaporating compounds which decompose into gaseous products prior to the onset of the
21 reaction of strontium carbonate.
- 22 225. The method as set forth in claim 224, wherein the volatile compound is selected from
23 the group consisting of elemental sulfur and ammonium carbonate included in a weight ratio
24 with strontium carbonate in the range of 1:9 to 1:1.
- 25 226. The method as set forth in claim 222 or 225, wherein the source of high purity
26 strontium carbonate is doped with a source of cerium in the range of 0.01 to 0.35 mole%.
- 27 227. The method as set forth in claim 96, wherein the strontium sulfide phosphor is
28 synthesized by a method comprising:
29 providing a source of high purity strontium carbonate in a dispersed form;
30 heating the strontium carbonate in a reactor with gradual heating up to a maximum
31 temperature in the range of 800 to 1200°C;
32 contacting the heated strontium carbonate with a flow of sulfur vapours formed by

1 heating elemental sulfur in the reactor to at least 300°C in an inert atmosphere; and
2 terminating the reaction by stopping the flow of sulfur at a point when sulfur dioxide or
3 carbon dioxide in the reaction gas reaches an amount which correlates with an amount of
4 oxygen in oxygen-containing strontium compounds in the reaction product which is in the
5 range of 1 to 10 atomic percent.

6 228. The method as set forth in claim 227, wherein the sulfur is heated in the temperature
7 range of 360 to 440°C.

8 229. The method as set forth in claim 227 or 228, wherein the strontium carbonate is
9 provided in a dispersed form by mixing with one or more volatile, non-contaminating, clean
10 evaporating compounds which decompose into gaseous products prior to the onset of the
11 reaction of strontium carbonate.

12 230. The method as set forth in claim 229, wherein the volatile compound is selected from
13 the group consisting of elemental sulfur and ammonium carbonate included in a weight ratio
14 with strontium carbonate in the range of 1:9 to 1:1.

15 231. The method as set forth in claim 227 or 230, wherein the source of high purity
16 strontium carbonate is doped with a source of cerium in the range of 0.01 to 0.35 mole%.

17 232. A method of forming a patterned phosphor structure having red, green and blue sub-
18 pixel elements for an AC electroluminescent display, comprising:

19 a) selecting at least a first and a second phosphor, each emitting light in different
20 ranges of the visible spectrum, but whose combined emission spectra contains red, green and
21 blue light;

22 b) depositing a layer of the first phosphor which is to form at least one of the red, green
23 or blue sub-pixel elements;

24 c) applying a photo-resist to the first phosphor, exposing the photo-resist through a
25 photo-mask, developing the photo-resist, and removing the first phosphor in regions that the
26 first phosphor is to define as one or more of the red, green and blue sub-pixel elements,
27 leaving spaced first phosphor deposits, wherein the first phosphor is removed with an etchant
28 solution comprising a mineral acid, or a source of anions of a mineral acid, in a non-aqueous,
29 polar, organic solvent which solubilizes the reaction product of the first phosphor with anions
30 of the mineral acid, and wherein optionally, prior to removing the first phosphor with the
31 etchant solution, the first phosphor layer is immersed in the non-aqueous organic solvent;

32 d) depositing the second phosphor material over the first phosphor deposits and in

- 1 regions which are to define the other of the red, green and blue sub-pixel elements; and
2 e) removing by lift-off, the second phosphor material and the resist from above the first
3 phosphor deposits leaving a plurality of repeating first and second phosphor deposits arranged
4 in adjacent, repeating relationship to each other.
- 5 233. The method as set forth in claim 232, wherein the lift-off step is accomplished using a
6 non-aqueous, predominately polar, aprotic solvent solution.
- 7 234. The method as set forth in claim 233, wherein at least one of the phosphors is an
8 alkaline earth sulfide or selenide phosphor, and wherein the etchant solution is a mineral acid
9 in methanol.
- 10 235. The method as set forth in claim 234, wherein the etchant solution includes an amount
11 between 0.1 and 10% by volume of the mineral acid.
- 12 236. The method as set forth in claim 235, wherein the mineral acid is mineral acid is HCl
13 or H_3PO_4 or mixtures of these acids.
- 14 237. The method as set forth in claim 235 or 236, wherein the photoresist is a negative
15 resist.
- 16 238. The method as set forth in claim 237, wherein the photoresist is a polyisoprene-based
17 photoresist.
- 18 239. The method as set forth in claim 235, 237, or 238, wherein the lift-off is accomplished
19 with a solution of methanol in toluene.
- 20 240. The method as set forth in claim 240, wherein the methanol is included in an amount
21 between 5 and 20% by volume.
- 22 241. The method as set forth in claim 235, 237, 238 or 240, wherein one of the phosphors is
23 a strontium sulfide phosphor.
- 24 242. The method as set forth in claim 241, wherein the first phosphor is a strontium sulfide
25 phosphor, and the second phosphor is a zinc sulfide phosphor.

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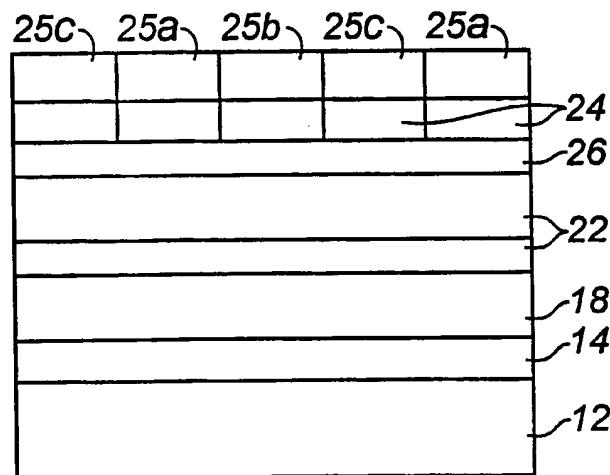


FIG. 1

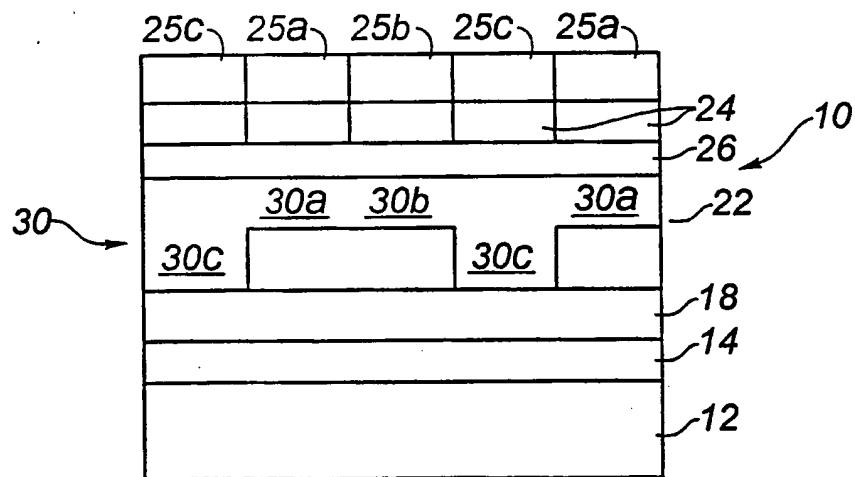


FIG. 2

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FIG. 3

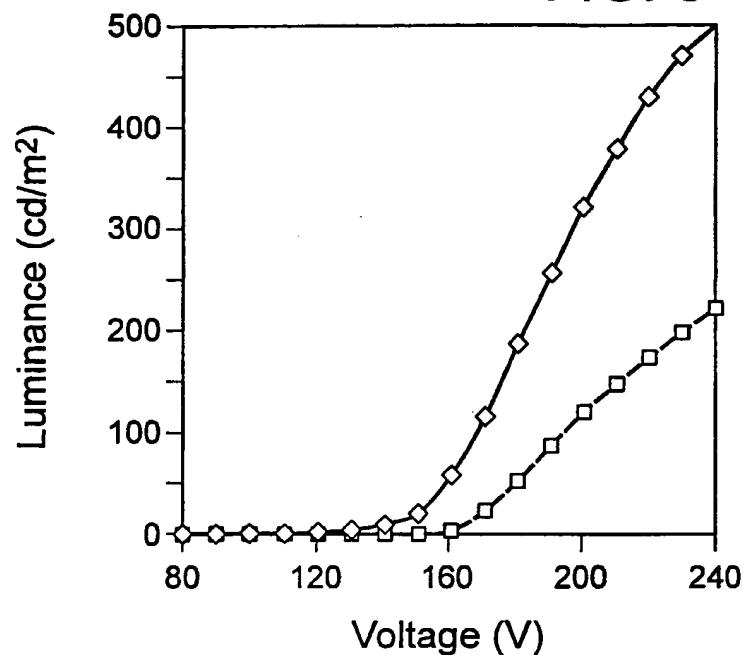
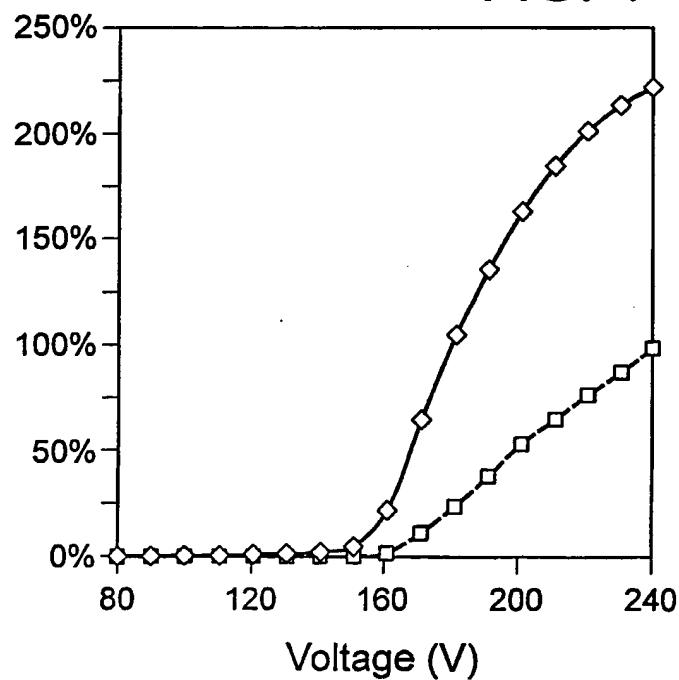


FIG. 4



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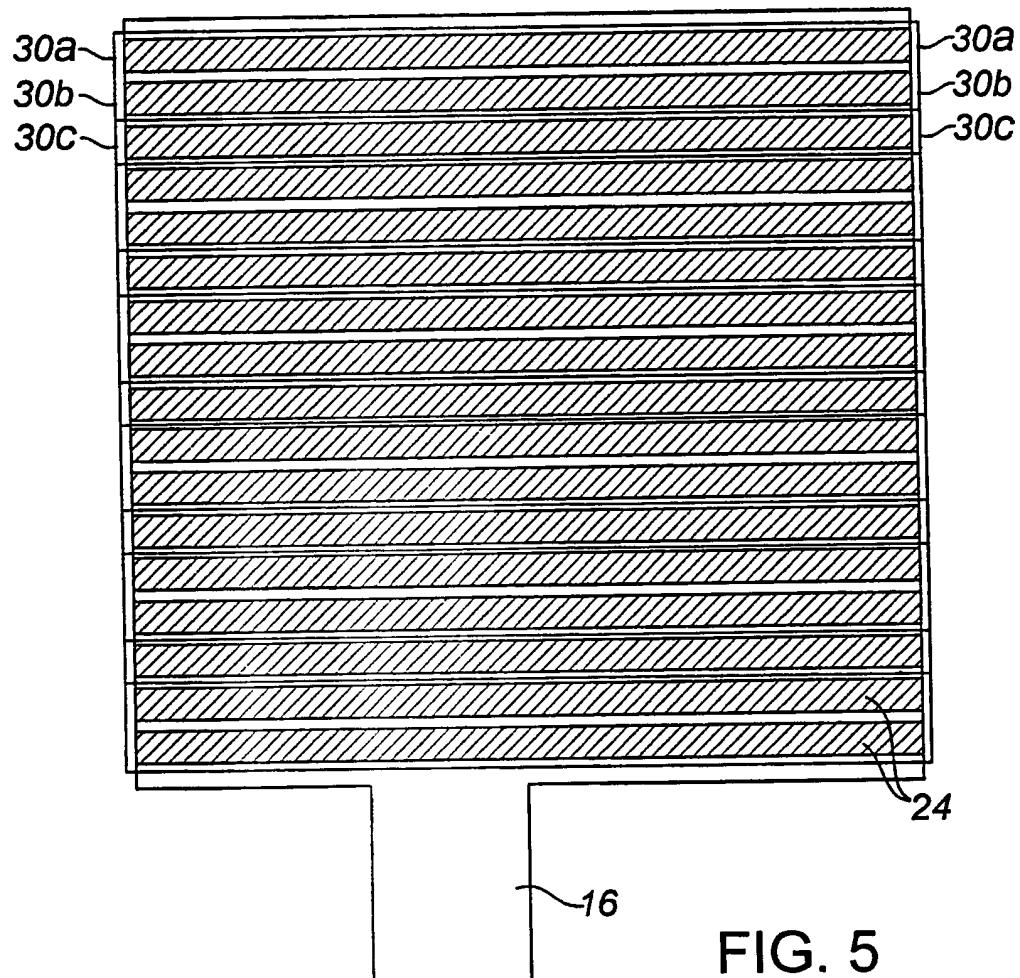


FIG. 5

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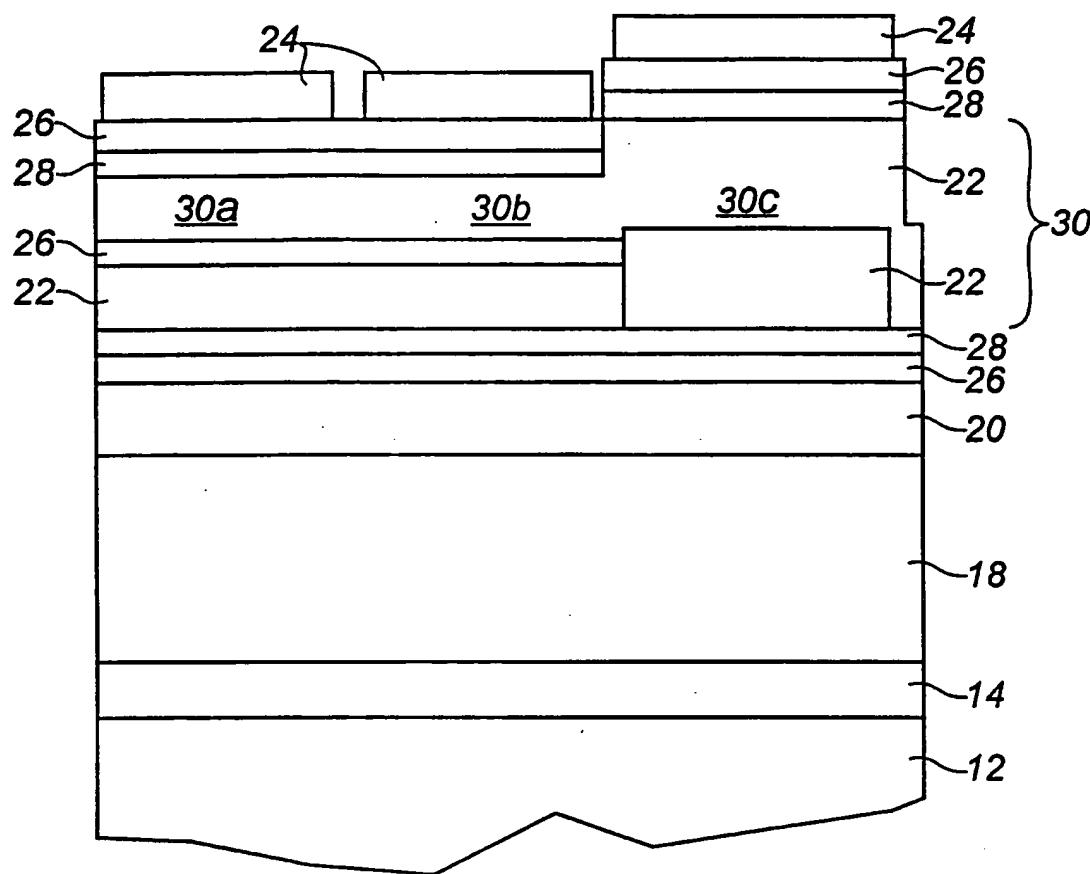


FIG. 6

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FIG. 7

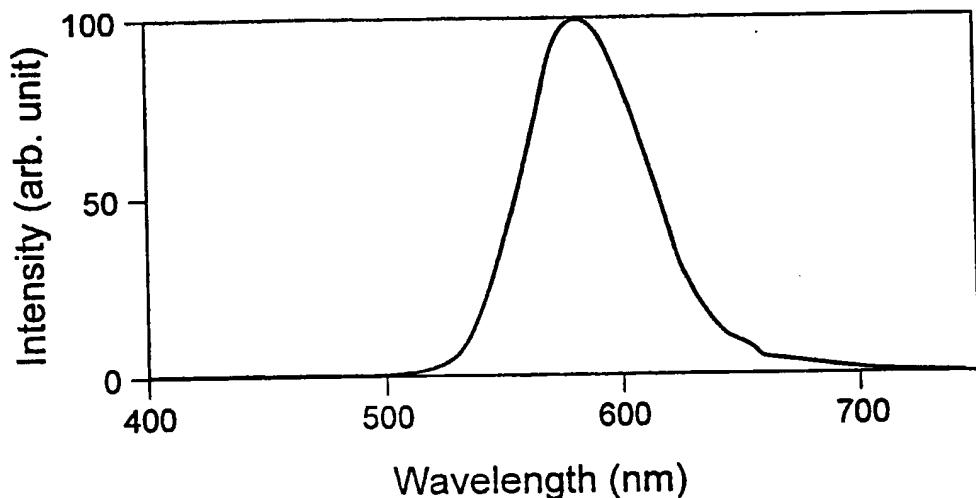
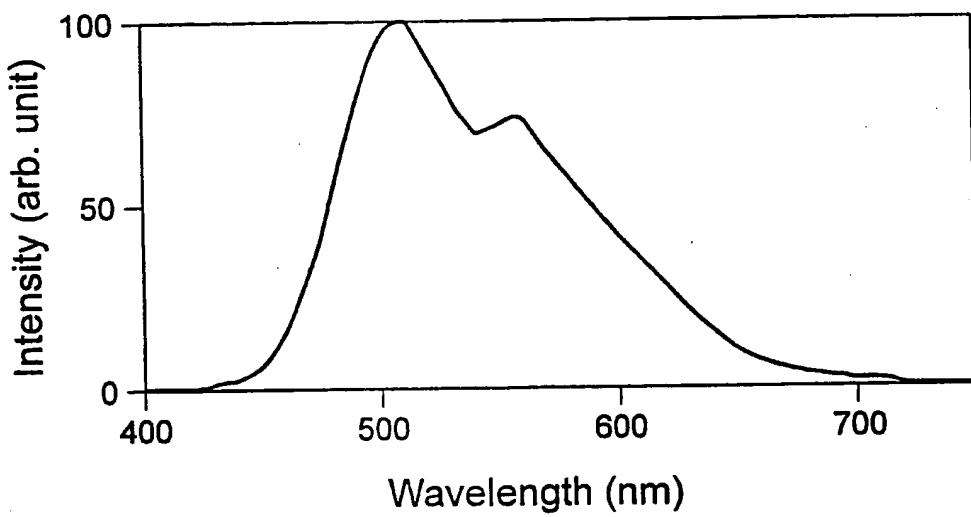


FIG. 8



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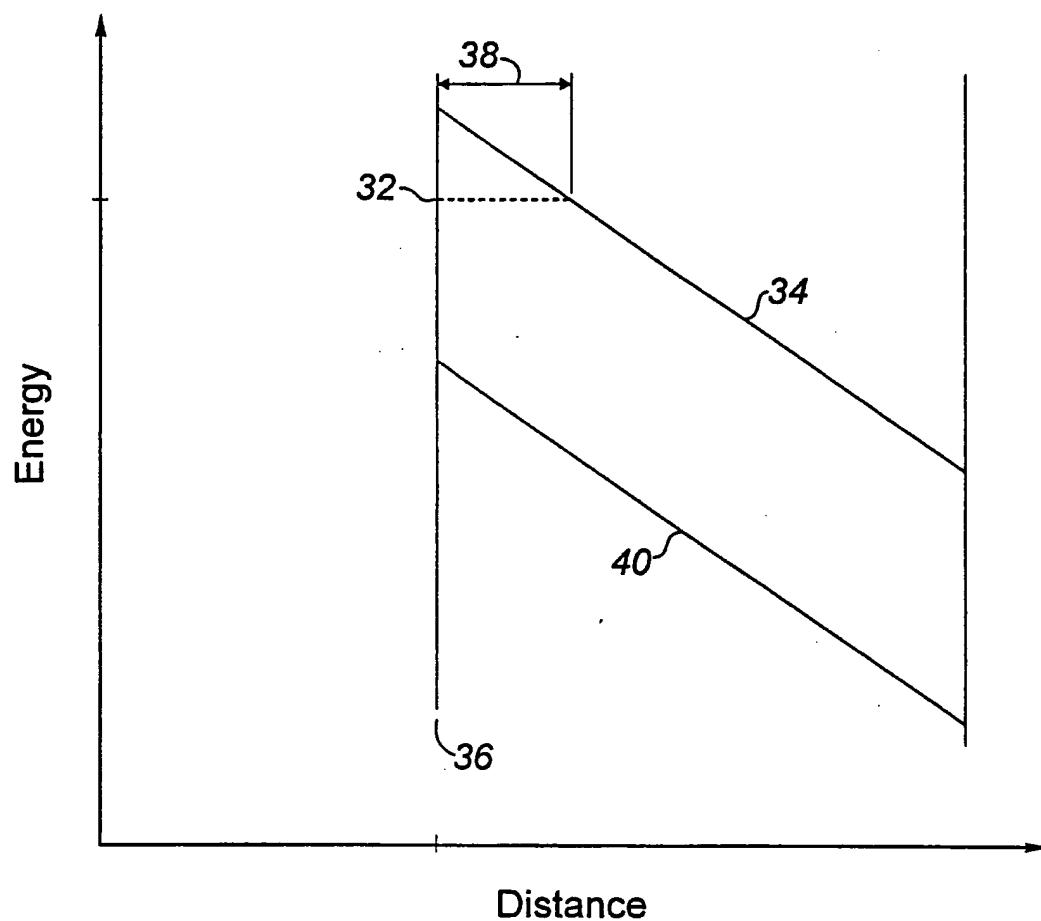


FIG. 9

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 00/00561

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 H05B33/14 H05B33/12 H05B33/10 H05B33/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, WPI Data, PAJ, IBM-TDB

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US 5 932 327 A (INOGUCHI KAZUHIRO ET AL) 3 August 1999 (1999-08-03) the whole document —	1-221
A	OKAMOTO F ET AL: "Preparation and cathodoluminescence of CaS:Ce and Ca/sub 1-x/Sr/sub x/S:Ce phosphors" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, FEB. 1983, USA, vol. 130, no. 2, pages 432-437, XP000915341 ISSN: 0013-4651 page 432 -page 437 —	222-231

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/CA 00/00561

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5932327 A	03-08-1999	JP 2850820 B JP 9097677 A	27-01-1999 08-04-1997

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